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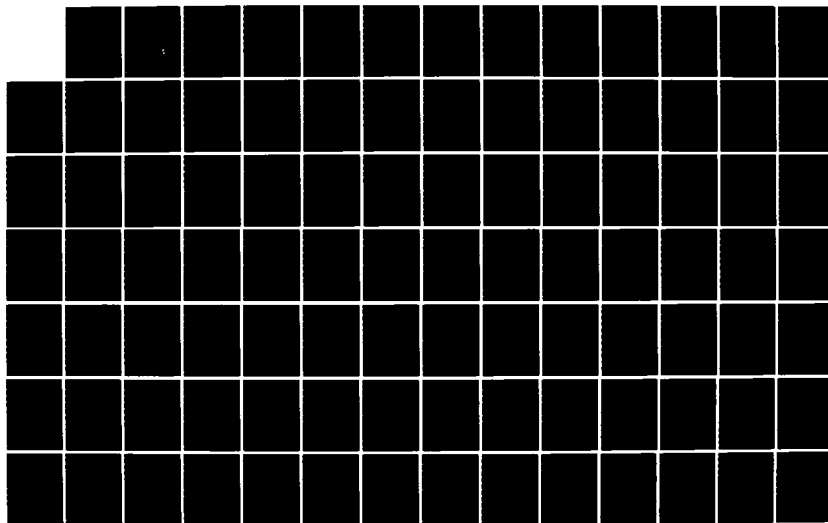
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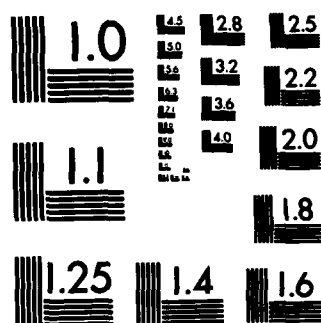
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METHODS FOR ESTIMATING PHYSICOCHEMICAL PROPERTIES OF INORGANIC CHEMICALS OF ENVIRONMENTAL CONCERN

FINAL REPORT, PHASE I

by

Warren J. Lyman, Ph.D.
Brian M. Barnett, Ph.D.

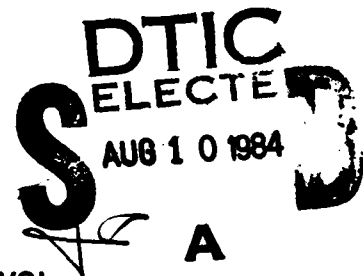
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Acorn Park
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Fort Detrick, Frederick, MD 21701

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This study was the first phase of a program designed to produce (in Phase II) a handbook which will provide information, including descriptions of calculational procedures or estimation methods, on environmentally important properties of inorganic and organometallic chemicals. The Phase I program evaluated the state-of-knowledge in this area and also assessed the capabilities and probable needs of environmental scientists and managers for guidance in this area. Outside experts were used in this process. This Phase I report provides a detailed outline and discussion of the handbook to be prepared in Phase II.		

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EXECUTIVE SUMMARY

This report describes the results of Phase I of a two-phase program being carried out by Arthur D. Little, Inc. for the U.S. Army Medical Bioengineering Research and Development Laboratory. The purpose of this program is to prepare a Handbook (the Phase II final report) which will provide details and recommendations on methods to estimate - or assess the importance of - environmentally important properties of inorganic and organometallic compounds.

The Phase I portion of the program was, essentially, a problem definition study to determine just what properties and processes, and what types or classes of inorganic compounds, should be covered in this Handbook. A further objective of Phase I was to determine the best way in which to present this information to the Handbook users, who are a relatively new group of environmental scientists and managers.

We obtained some general guidance (and inspiration) in our Phase I work from our Handbook of Chemical Property Estimation Methods - [The Environmental Behavior of Organic Compounds] (McGraw-Hill, 1982), which was initially prepared for the U.S. Army. However, we were careful not to let the "organics" Handbook restrain our thinking for the proposed "inorganics" Handbook. The former was essentially limited to a description of estimation methods for the environmentally important properties that were estimable. For the latter, we are proposing a broader coverage of all (key) environmentally important properties and processes, whether or not they are estimable. (If a property is estimable, then the estimation methods will be covered in a fashion similar to those in the "organics" Handbook.) In addition, we are proposing a major section which will provide environmentally important property data for a variety of inorganic elements, ligands and compounds.

Table 1 is a summary outline of the proposed Handbook. Part I will provide a generic description of processes and properties; it will - to the extent possible - provide specific instructions to assist users in estimating property values and/or assessing the importance of a particular property or process. Where estimation (or even assessment) is difficult or impossible, special help will be provided in the form of tabulated data, illustrations and examples to demonstrate the range of possibilities. Part I will also contain major sections on uptake by biota and environmental fate models.

Part II of the Handbook will present environmentally important property data for several groups of elements or compounds: (a) major elements and ligands of the earth's crust and surface waters; (b) pollutant metals; (c) pollutant ligands; (d) radionuclides; and (e) selected chemical classes. In each case, data will be provided for specific elements, ligands or compounds along with text describing, where pertinent, how groups or classes generally behave in the environment.

The need for this two-part approach was identified relatively early in our Phase I work, during an all-day meeting with key Arthur D. Little, Inc. case team members, our extramural consultants, and the U.S. Army Project Officer. We expect that it will prove especially valuable to environmental scientists and managers in preparing timely analyses of existing or potential environmental problems.

TABLE 1

INORGANIC HANDBOOK OVERVIEW/OUTLINE

The major sections and subsections being proposed are:

- FRONT MATTER
[Including guide to use of book]
- PART I - GENERIC DESCRIPTION OF PROCESSES AND PROPERTIES
 1. Transport and Transformation Processes
 2. Estimations Associated with Equilibrium Conditions
 3. Estimations Associated with Process Kinetics
 4. Uptake by Biota
 5. Models for Prediction of Environmental Fate
- PART II - THE ENVIRONMENTAL PROPERTIES OF IMPORTANT ELEMENTS AND CHEMICAL CLASSES
 6. Major/Matrix Elements
 7. Trace or Pollutant Metals
 8. Trace or Pollutant Ligands
 9. Radionuclides
 10. Chemical Classes (Organometallics plus up to 17 other classes)
- APPENDICES
[Several suggested, including one with data on natural concentrations of elements in the environment.]
- SUBJECT INDEX

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	2
I. INTRODUCTION	9
A. Background	9
B. Need for Guidance	9
C. The Phase I Program	11
D. Overview of Phase I Report	11
II. OBJECTIVES OF PHASE II HANDBOOK	13
III. PROPOSED OUTLINE OF INORGANICS HANDBOOK	15
A. Overview	15
1. Content of Part I	15
2. Content of Part II	18
3. Other Supporting Sections	21
B. Detailed Outline	21
IV. DISCUSSION OF HANDBOOK OUTLINE, CONTENTS, APPROACH	30
o PART I - GENERIC DESCRIPTION OF PROCESSES AND PROPERTIES	30
1. Transport and Transformation Processes	31
2. Estimations Associated with Equilibrium Conditions	33
a. Introduction	33
b. Gas Adsorption on Solids	33
c. Acid-Base Equilibria and Hydrolysis	36
d. Ligand Formation	40
e. Electron Transfer: Oxidation/Reduction	44
f. Adsorption/Uptake	48
g. Volatilization	53
h. Radioactive Processes and Properties	55
i. Microbial Transformation of Inorganic Pollutants	60
3. Estimations Associated with Process Kinetics	62
a. Description of Property	62
b. Mathematical Representation	62
c. Related Environmental Scenarios	64
d. Quantitative Applications in Environmental Problems	65
e. Estimation of Environmental Quantities Based on Process Kinetics	66

CONTENTS (continued)

	<u>Page</u>
4. Uptake by Biota	70
a. Purpose	70
b. Content	70
5. Models for the Prediction of Environmental Fate	74
a. Objectives	74
b. Summary of Overall Approach	74
c. Description of Proposed Sections	75
o PART II - THE ENVIRONMENTAL PROPERTIES OF IMPORTANT ELEMENTS, LIGANDS AND CHEMICAL CLASSES	80
Overview	81
6. Major/Matrix Elements and Ligands	81
a. Properties and Speciation in Water	82
b. Properties and Speciation in Soil	82
7. Trace or Pollutant Metals	83
a. Coverage	83
b. Information to be Provided for Each Metal	87
8. Trace or Pollutant Ligands	87
a. Coverage	87
b. Information to be Provided	88
9. Radionuclides	90
10. Chemical Classes	94
a. Overview	94
b. Organometallic Compounds	99
APPENDICES	107
A. Sources of Measured Data	107
B. Natural/Background Concentrations of Elements and Other Inorganic Species	107
C. Description of Soil Types and Properties	107
D. Pollutant Criteria or Standards	113

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Inorganic Handbook Overview/Outline	3
2. Inorganic Handbook Overview/Outline	16
3. Properties and Processes to be Covered in Sections 1 and 2 of Handbook	17
4. List of Element Groups and Ligands to be Covered in Handbook	19
5. Chemical Classes to be Covered	20
6. Inorganics Handbook Outline	22
7. Terrestrial Biota: Uptake by Plants, Normal Conditions (Example Table Format)	71
8. Terrestrial Biota: Uptake by Plants, Problematic Conditions (Example Table Format)	72
9. The Occurrence of Metals in Various "Regulatory" Lists	84
10. Predominant Inorganic Species for Several Trace Metals in Aquatic Systems	85
11. Some Radionuclides from the Natural Decay of 238-Uranium	91
12. Selected Radionuclides with Half-Lives Greater Than 1 Year	92
13. Examples of Chemicals in Chemical Classes Chosen	95
14. Organometallics with Threshold Limit Values	101
15. Organometallics on RCRA Listing of Hazardous Wastes	101
16. Organometallics Used as Insecticides, Fungicides, Herbicides, Fumigants, Growth Regulators, Repellents, and Rodenticides	102
17. Organometallics Listed as TSCA Section 4 Chemicals	103
18. Organometallics Listed as TSCA Section 5 Chemicals (Selected Examples)	103
19. Natural/Background Concentration of Elements and Other Inorganic Species	107
20. Unified Soil Classification System	112
21. Regulations (Standards and Criteria) Affecting Inorganics and Organometallics	114
22. Standards/Criteria Applicable to Inorganics and Organometallics	116

LIST OF FIGURES

	<u>Page</u>
1. Adsorption of Various Gases as a Function of Normal Boiling Point	35
2. Characteristic Rate Constants for Substitution of Inner Sphere H_2O of Various Aquo Ions	68
3. Example Matrix for Sources of Measured Data	108
4. USDA Textural Classification Chart	111
5. Comparison of USCS and USDA Particle-Size Scales	111

I. INTRODUCTION

A. BACKGROUND

The last 15 years have brought an ever-growing awareness in this country of the need for environmental protection, especially where the use of chemicals is involved. The decade of the 1970s was especially important in the United States for the passage of key federal acts or actions that mandate a minimum level of protection. Included were the following:

- National Environmental Policy Act (1969)
- Creation of the U.S. Environmental Protection Agency (1970)
- Occupational Safety and Health Act (1970)
- Clean Water Act Amendments (1972)
- Marine Protection Research and Sanctuaries Act (1972)
- Safe Drinking Water Act (1973)
- Toxic Substances Control Act (1976)
- Resource Conservation and Recovery Act (1976)
- EPA/NRDC Settlement Agreement on Toxics ("Priority Pollutants") (1976)
- Clean Water Act Amendments ("Toxics" added) (1977)
- Comprehensive Emergency Response, Compensation and Liability Act (Superfund) (1980)

In addition, state and local authorities have passed their own laws or bylaws covering related subjects.

As a result of this heightened concern and regulatory activity, there has emerged - of necessity - a legion of environmental scientists and managers responsible for the development and implementation of regulations, for research into control technologies, for the operation of pollution control facilities, etc. It is likely that they number in the several tens of thousands. (The U.S. Environmental Protection Agency alone has nearly 10,000 employees.)

B. NEED FOR GUIDANCE

There is a real need today for a wide variety of guidance manuals to assist these environmental scientists and managers in government, industry and universities in carrying out their work. These individuals come to their positions with varied training (e.g., from a B.S. in biology, to an M.S. in civil engineering, to a 20-year job as a chemical process engineer), little of which is directed toward helping them make timely decisions related to environmental protection where toxic chemicals are involved.

Manuals are now available for designing wastewater treatment plants, cleaning up oil spills, monitoring stack gas emissions, and preparing river management plans, for example; however, there is virtually no guidance on how to assess the very complex problems that relate more

directly to the fate and transport of chemicals in the environment. What are needed are: (a) guidance on assessing what physicochemical properties and processes are environmentally important, (b) guidance on using the properties to maximum advantage, and (c) some actual values of these properties. In 1982 we prepared a Handbook designed to fill part of this need by providing a compilation of carefully described estimation methods for environmentally important properties of organic chemicals. The need for estimation methods was described in the introduction to this "organics" Handbook as follows:

"Over the past decade, the chemical contamination of our environment has justifiably aroused growing concern. A proper assessment of the risk - to man and the environment - created by exposure to these chemicals generally includes attempts to measure or predict the concentrations in various environmental compartments in conjunction with toxicological data. Frequently, however, neither the concentration data nor the toxicological data are adequate for any realistic assessment. In addition, basic physical and chemical data are often unavailable, especially for new organic chemicals being considered for bulk manufacture. If, however, the most important physical and chemical properties of these chemicals could be estimated, their transport and fate in the environment could be better understood - even modeled in some cases - and the eventual environmental concentrations might be estimated."

It was clear at the time the "organics" Handbook was prepared that a separate program, and perhaps quite a different Handbook, would also be required for the coverage of inorganic chemicals and special classes such as organometallics. The current program was instituted to fill this need.

Because of several important differences between inorganic and organic chemicals, the respective Handbooks require different approaches and content:

- One obvious distinction is the number and variety of elements involved. The organics are primarily composed of carbon and hydrogen with lesser amounts of oxygen, nitrogen, sulfur, phosphorus and halides (Cl, Br, I, F); the inorganics cover essentially all compounds where carbon is not the basic element. The variety of atom combinations and type of bonds is vastly more complex for the full range of inorganic compounds, which may contain any of 30 - 50 different elements.
- A second distinction is the type of bonding involved: organic chemicals of environmental concern are commonly neutral, i.e., non-ionizing in aqueous solution, but many inorganics dissociate into ionic species when dissolved in water.

*-----
Note that all references to the "inorganics" Handbook refer to the final report to be prepared in Phase II of this program.

- Finally, this complexity in elemental composition and bond nature makes physicochemical property prediction difficult, if not beyond the scope of current capabilities. By contrast, many properties of (neutral) organic chemicals are relatively simple functions of molecular mass, volume and interaction terms reflecting, for example, the electro-negativity or hydrogen bonding potential of functional groups.

C. THE PHASE I PROGRAM

Phase I of this program was designed to be a problem definition study, i.e., to assess just what properties and processes needed to be covered, which of these could be estimated, and how they should be covered. The key output of Phase I is, essentially, a detailed description of the contents of the Phase II Handbook.

In approaching the Phase I task, we faced two major issues. One is the extreme breadth and complexity of the subject ("inorganic chemistry"); the other is the lack of any easy (or scientific) way to assess the needs of the community of environmental managers and scientists we seek to serve. As a start, we interviewed a number of extramural experts and examined recently published books covering the subject area. Very useful inputs came from two meetings of the key ADL project team members, the U.S. Army Project Officer, and one or more of the four extramural consultants we had chosen to assist us. These consultants were:

- Dr. Marc Anderson, University of Wisconsin
- Dr. Donald Langmuir, Colorado School of Mines
- Dr. Albert Page, University of California, Riverside
- Dr. Lee Sommers, Purdue University

The two meetings, held in October and December 1983, provided an opportunity for careful consideration of the basic goals and objectives of the Handbook and resulted in the identification of the need for certain sections. Much of the subsequent work by Arthur D. Little, Inc. in Phase I involved expanding or refining the rough outline that emerged from these meetings.

Once the outline had been fairly well established, we focused on specific topics to determine in greater detail just what information, data and/or estimation methods were available and how to present them.

D. OVERVIEW OF PHASE I REPORT

Section II of this report provides additional information on the specific objectives of Phase II and the Handbook it will produce.

Section III contains the proposed outline of the Handbook; both an overview and a detailed outline are provided.

Section IV discusses most of the key sections proposed for the Handbook. These generally provide information relating to the environmental importance of a property, process or chemical and a description of how the subject will be treated in the section, based upon our understanding of the users' needs and available information, estimation methods and/or data.

II. OBJECTIVES OF PHASE II HANDBOOK

Our main objective in Phase II is to produce a comprehensive, easy-to-use handbook to help environmental scientists and managers assess the environmental fate and transport of inorganic and organometallic compounds. These individuals may face situations or scenarios such as the following:

- NPDES, FIFRA, RCRA (etc.) permit applications
- R&D for wastewater treatment (e.g., metal removal)
- Modeling or assessment of chemical spills
- Modeling or assessment of soil/groundwater contamination
- Modeling the speciation and fate of metals in water
- Assessment of the consequences of agricultural use of various chemicals
- Assessment of land treatment of hazardous wastes or land application of municipal wastes or sewage sludge
- Assessment of environmental releases of pollutants to all media
- Remedial action at old chemical dump sites
- Premanufacture Notice (PMN) review
- Assessment of potential food contamination incidents
- Utilization of wastes
- Migration of food additives
- Ocean disposal
- Coal combustion
- Assessing impacts of acid rain.

In each case there may be a variety of naturally occurring and pollutant chemical species to contend with, several fate and transport pathways to consider and a host of environmental variables (e.g., temperature, pH, Eh, soil types) with which to contend. Where can the scientist or manager turn to for help today? Aside from undertaking costly and lengthy research or field studies to obtain specific answers, little reliable guidance is easily and quickly available. Our Handbook should help to meet this need.

The specific subject coverage of the Handbook is described in Sections III and IV of this report and will not be repeated here. Rather, we wish to reiterate some of the underlying goals and objectives. A background discussion leading to a statement of need for the Handbook was given in Section I.

First, we expect to emphasize usefulness, readability, and ease of use. We are aware of the limited training and experience of most environmental managers, in the sense that one individual is seldom qualified to assess all (or even most) of the environmental processes and transport pathways that may lead to inadvertent or excessive environmental exposure. These individuals need clear guidance, which can be provided in a handbook that has been carefully organized and clearly written, contains step-by-step instructions for the use of models and estimation methods, and provides illuminating examples that are pertinent to their problems.

Many books are available today on environmental chemistry, some focusing on organic chemicals, some on inorganic chemicals, and some on both. Most of these books appear to fall into one of the following categories: (a) a compilation of works by several authors (e.g., a collection of papers from a symposium); (b) college or graduate-level textbooks written by professors for their students; (c) monographs focusing on the environmental chemistry of a single medium (e.g., air, water, or soil); or (d) other specialized books (e.g., on modeling, special classes of chemicals, or special treatment processes such as land farming). We know of none that is clearly designed to help in problem solving; most are difficult to use unless the reader is already knowledgeable in the subject. One of our basic objectives is to differentiate the Handbook from these texts.

A second major objective concerns credibility, i.e., the reliability accorded the Handbook by the user. We hope to achieve a high degree of reliability by making sure that the information is near state-of-the art in scientific understanding without being too specialized or academic. Proper examples will be given, and full referencing will make it an authoritative reference resource. All work will go through a careful series of checks, by our internal reviewers and editor as well as by extramural reviewers, to ensure completeness and correctness.

Nevertheless, we expect to have to make hard, practical decisions about the depth or extent of coverage in many areas. No Handbook could provide all the answers that an environmental manager, not to mention a specialist, may need. We intend that our Handbook should be the first reference the environmental scientist or manager consults when addressing a new problem, and that it provide sufficient guidance for most preliminary assessments (e.g., of potential environmental exposure and risk), so that prompt action can be taken while more detailed scientific data and advice are sought.

III. PROPOSED OUTLINE OF INORGANICS HANDBOOK

A. OVERVIEW

Table 2 is a one-page summary outline of the proposed Handbook. The key feature of this outline is the division into two major parts, the first providing a generic description of environmentally important properties and processes and the second describing the environmental properties of important elements and chemical classes. There will be numerous cross-references between Parts I and II.

This two-part approach was suggested early in our Phase I study, during the initial meeting with the extramural consultants. Further study only confirmed the need for such an approach. Some Handbook users, for example, may wish only to understand how a certain property or process (e.g., oxidation) might affect the fate of metals; others may only want information (e.g., oxidation states) on a specific metal. Some will want both.

1. Content of Part I

Part I of the Handbook will present a basic (generic) description of each important property and process - its importance to environmental studies, the mathematical equations in which it is used (i.e., the primary equilibrium and rate equations associated with the property), and any estimation methods that are available. If estimation methods are not available, as will often be the case, other help will be given to the user in the form of graphs, tables or verbal descriptions of the range of values to be encountered. Examples will be provided in all cases.

The properties or processes selected for coverage in the Handbook are listed in Table 3. The equilibrium-related aspects of the properties selected will be covered in Section 2; the kinetics (i.e., rates, rate constants) of the related processes will be covered in Section 3. These major sections will contain extensive scientific descriptions, written in a form suitable for environmental scientists and managers. To help these users, Section 1 will summarize the important transport and transformation processes for various scenarios (land disposal, surface water discharge, organometallics in air, etc.). This will lead to an identification of the important properties/processes involved in each scenario, accompanied by specific references to other pertinent sections of the Handbook.

Section 4 of the Handbook will cover uptake by biota (plants, terrestrial animals, fish). The ultimate concern of the environmental scientist or manager will usually be the impact on humans and other life forms; while this section will not specifically cover toxicology, it will cover uptake and, where available, criteria for limiting uptake in biota.

TABLE 2

INORGANIC HANDBOOK OVERVIEW/OUTLINE

The major sections and subsections being proposed are:

- FRONT MATTER
[Including guide to use of book]
- PART I - GENERIC DESCRIPTION OF PROCESSES AND PROPERTIES
 1. Transport and Transformation Processes
 2. Estimations Associated with Equilibrium Conditions
 3. Estimations Associated with Process Kinetics
 4. Uptake by Biota
 5. Models for Prediction of Environmental Fate
- PART II - THE ENVIRONMENTAL PROPERTIES OF IMPORTANT ELEMENTS AND CHEMICAL CLASSES
 6. Major/Matrix Elements
 7. Trace or Pollutant Metals
 8. Trace or Pollutant Ligands
 9. Radionuclides
 10. Chemical Classes (Organometallics plus up to 17 other classes)
- APPENDICES
[Several suggested, including one with data on natural concentrations of elements in the environment.]
- SUBJECT INDEX

TABLE 3
PROPERTIES AND PROCESSES TO BE COVERED
IN SECTIONS 1 AND 2 OF HANDBOOK

Gas Phase, Homogeneous

- Oxidation: $X + O_2 \rightarrow Y$
- Photochemical: $X + h\nu \rightarrow Y$

Gas Phase \rightarrow Liquid or \rightarrow Solid

- Droplet formation: $X + H_2O \rightarrow Y$ (liq.)
- Solid particulate formation: $X + H_2O \rightarrow Y$ (solid)
- Adsorption onto solids: $X + \text{particulate} \rightarrow X$ (ads)

Speciation

- Calculation of activity coefficients
- Acid-base equilibria and hydrolysis: $X + H_2O \rightarrow XOH + H$
- Ligand formation: $X + nL \rightarrow XL_n$
- Electron transfer, oxidation/reduction: $X^+ + Y^- \rightarrow Z$
- Precipitation: $X + Y \rightarrow Z$ (solid)
- Dissolution /solubility: Z (solid) $\rightarrow X + Y$
- Steps in speciation calculations

Additional Processes of Interest

- Adsorption/uptake: $X + \text{Solid} \rightarrow X\text{-Solid}$
- Volatilization: X (liquid) $\rightarrow X$ (gas)
- Photolysis, free radical oxidation: $X + h\nu \rightarrow Y$
- Polymerization: $nX \rightarrow X_n$

Radioactive Processes and Properties

- Recoil transport
- Elemental transmutation
- Sequential decay

Microbial Transformations

Section 5 will provide "user-friendly" descriptions of useful and available models that predict the speciation and transport of inorganics in the environment. Specific guidance will be given on scenarios of interest, model selection, and model capabilities and limitations.

2. Content of Part II

Part II of the Handbook will contain chemical-specific data and information relating to environmentally important properties of inorganic chemicals. The data will vary with the elements or compounds discussed but will generally be associated with the processes described in Sections 2 and 3.

The data will thus focus on those properties (e.g., equilibrium distribution coefficients and rate constants) that the user must know in order to understand the fate and transport of a chemical in the environment, or those needed as inputs to the models described in Section 5. Tables 4 and 5 summarize the elements, ligands and chemical classes to be covered.

Section 6, which begins Part II, will deal with the major or matrix elements (e.g., Na, K, Ca, Mg, Si, Al, Fe) and ligands (OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) in water and soil environments. These species essentially define the basic water chemistry in most natural waters and thus influence the speciation and fate of trace pollutants. The behavior and speciation of these major elements and ligands will be described in a way that will clarify the factors controlling trace pollutant fate.

Section 7 will cover trace or pollutant metals or metalloids such as Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Se, Ag, Tl and Zn. Subsections will provide data on properties of the elements and fate processes in fresh water, seawater and soil.

Section 8 will cover trace or pollutant ligands such as CN^- , NH_4^+ , Br^- , S^{2-} , and PO_3^{3-} . Data will be provided on the speciation of these ligands (i.e., the types of compounds formed and their stability), their natural cycles, and their fate in water and soil environments.

Section 9 will provide data on the important radionuclides, both naturally occurring (e.g., 226-Ra and 238-U) and artificial (e.g., 99-Tc, 90-Sr, 60-Co). In addition to data related to their radioactivity (type of radiation emitted, half-life, daughter products, etc.), we will also provide data on properties relating to speciation and environmental fate, as with the trace or pollutant metals.

Section 10, the last major section, will provide data on chemical classes of interest. At present we have identified ten major and eight minor classes that may be covered. Included in the majors, for example, are organometallics, acids, and oxides; the full list of

TABLE 4
LIST OF ELEMENT GROUPS AND LIGANDS
TO BE COVERED IN HANDBOOK

Major/Matrix Elements

Sodium
 Potassium
 Calcium
 Magnesium
 Silicon
 Aluminum
 Iron

Major/Matrix Ligands

Hydroxyl (OH^-)
 Chloride (Cl^-)
 Sulfate (SO_4^{-2})
 Carbonate (CO_3^{-2})
 Bicarbonate (HCO_3^-)
 Sulfide (S^{-2})

Trace or Pollutant Metals

Antimony	Lead
Arsenic	Mercury
Barium	Manganese
Beryllium	Nickel
Cadmium	Selenium
Chromium	Silver
Copper	Thallium
	Zinc

Trace or Pollutant Ligands

Nitrogen-containing (CN^- , NH_4^+ , NO_3^- , NO_2^-)
 Sulfur-containing (S^{-2} , $\text{S}_2\text{O}_3^{-2}$, SCN^- , SO_3^{-2} , SO_4^{-2} , HS^-)
 Phosphorus-containing (PO_4^{-3} , HPO_3^{-2} , Polyphosphates)
 Fluoride
 Bromide

Radionuclides

[Specific elements to be determined later]

TABLE 5

CHEMICAL CLASSES TO BE COVERED

<ul style="list-style-type: none"> • Organometallics • Acids • Anionics • Salts • Oxides • Gases 	<p><u>Major Classes</u> based on properties and/or constituents</p>
<ul style="list-style-type: none"> • S-Containing • P-Containing • Si-Containing • B-Containing 	<p><u>Major Classes</u> based on compounds of a specific element</p>
<ul style="list-style-type: none"> • Bases (Hydroxides) • Carbonyls • Carbides • Cyanides • Hydrides • Hypochlorites, Chlorates • Peroxides • Binary Compounds * 	<p><u>Minor Classes</u> based primarily on constituents</p>

* Binary compounds are those containing only two elements.

classes proposed is shown in Table 5. The data provided for each class will reflect the unique properties of that class with regard to environmental speciation, reactivity and general behavior.

We recognize that the current selection of elements, ligands, and chemical classes involves some overlap and/or duplication. This will be eliminated during the initial part of Phase II. In addition, some modification of the elements, ligands and classes listed may be required.

3. Other Supporting Sections

- Front Matter - In addition to a standard table of contents, list of tables and list of figures, we will provide a brief guide (in both graphic and textual form) to the use of the Handbook.
- Appendices - The list of desired appendices is not complete as yet; at a minimum, it will include one covering the natural (or background) concentrations of the elements in various environmental compartments and another describing various soil types and environmentally important soil properties. Others dealing with data sources and pollutant criteria are planned.
- Subject Index - A subject index will cover all major sections of the Handbook.

B. DETAILED OUTLINE

Table 6 is a detailed outline of the proposed inorganics Handbook. Some annotation is provided in this outline to clarify the intended content. The major components of each section and subsection are discussed in Section IV of this report.

TABLE 6

INORGANICS HANDBOOK OUTLINE

• FRONT MATTER

- Executive Summary
- Guide to Use of Handbook
- Acknowledgements
- Table of Contents
- List of Tables
- List of Figures

• PART I - GENERIC DESCRIPTION OF PROPERTIES AND PROCESSES

1. Transport and Transformation Processes

This Section will help the user identify the important transport and transformation processes for a variety of scenarios; cross references will be provided to other sections for detailed information.

- 1.1 Overview - with flowcharts
- 1.2 Air-Mediated - general description
- 1.3 Liquid-Mediated - general description
- 1.4 Soil/Sediment-Mediated - general description
- 1.5 Spontaneous (Radioactive decay)

2. Estimations Associated with Equilibrium Conditions

The following topics will be discussed for each of the properties/processes covered, as appropriate:

- A general discussion of the property and its environmental importance;
- Methods and ease of measurement (very brief);
- Key mathematical representations of the associated parameters (e.g., equilibrium constants, adsorption capacity);
- Probable range of values under environmental conditions;
- Effects of temperature, ionic strength and other variables on the property/process;
- Tabulations or plots of data illustrating the effect of various conditions for various chemical species;
- Methods (if any) for estimating the property and/or qualitative rules for assessing the likely importance of the property/process for a given chemical species;
- Sample calculations involving the property;
- References to other descriptions of the property;
- References to tabulations of data.

TABLE 6 (continued)

- 2.1 Gas Phase, Homogeneous
 - 2.1.1 Oxidation: $X + O_2 \rightarrow Y$
 - 2.1.2 Photochemical transformation: $X + h\nu \rightarrow Y$
- 2.2 Gas Phase \rightarrow Liquid or \rightarrow Solid
 - 2.2.1 Droplet formation: $X + H_2O \rightarrow Y$ (liq.)
 - 2.2.2 Solid particulate formation: $X + H_2O \rightarrow Y$ (solid)
 - 2.2.3 Adsorption onto solids: $X + \text{particulate} \rightarrow X$ (ads.)
- 2.3 Speciation
 - 2.3.1 Introduction/overview
 - 2.3.2 Calculation of activity coefficients
 - 2.3.3 Acid-base equilibria and hydrolysis + other
Dissociations:
 $X + H_2O \rightarrow XOH$
 - 2.3.4 Ligand formation: $X + nL \rightarrow XL_n$
 - 2.3.5 Electron transfer: oxidation/reduction:
 $X^+ + Y^- \rightarrow Z$
 - 2.3.6 Precipitation: $X + Y \rightarrow Z$ (solid);
dissolution/solubility: Z (Solid) $\rightarrow X + Y$
 - 2.3.7 Steps in speciation calculations
- 2.4 Additional Processes of Interest
 - 2.4.1 Adsorption/uptake: $X + \text{Solid} \rightarrow X\text{-Solid}$
 - 2.4.2 Volatilization: X (liquid) $\rightarrow X$ (gas)
 - 2.4.3 Photolysis, free-radical oxidation: $X + h\nu \rightarrow Y$
 - 2.4.4 Polymerization: $nX \rightarrow X_n$
- 2.5 Radioactive Processes and Properties
 - 2.5.1 Recoil transport
 - 2.5.2 Elemental transmutation
 - 2.5.3 Sequential decay
- 2.6 Microbial transformations
- 3. Estimations Associated with Process Kinetics
 - 3.1 Classification of Rates, e.g.:
Rapid (R): $t_{1/2} < 1 \text{ sec}$
Intermediate (I): $t_{1/2} = 1 \text{ sec} - 1 \text{ year}$
Slow (S): $t_{1/2} > 1 \text{ year}$
N.A. - no info. available
N.C. - not of concern
 - 3.2 Classification of Rates for Chemical Groups
For each type of reaction identified in Section 2 above, data on rate constants will be reviewed for various groups or classes of chemicals, including - if possible- those described in Part II. A matrix will then be prepared, with associated text, that classifies each chemical group/reaction matrix element according to the scheme described in Section 3.1 above (i.e., R, I, S, NA, NC,...)

TABLE 6 (continued)

Group *	Reaction Type (per Section 2)					
	Gas Phase		Liquid Phase, Homogeneous			
	Oxid.	Photol.	Hydrol.	Ligand	Polym.	...
1)	R	NA	NC	I	NC	
2)	R	I	R	R	S	
3)						
4)						

* Groups may be by periodic-chart groupings, by molecular class (e.g., organometallics with sigma bonds), and/or by phase (solid, liquid, gas).

3.3 Estimation of Reaction Rates

For each matrix element of the above table where rates are important (i.e., I or S), a discussion will be provided on:

- The availability of data
- Available estimation methods (if any)
- Discussion of environmental effects (temperature, catalysts, solvent, cosolutes)
- Sample calculations

4. Uptake by Biota

4.1 Introduction

Discussion of pathways, starting information, approaches, limitations, available data, other general concerns

4.2 Discussion of Uptake and Loss Processes

A scientific discussion of current understanding of the processes involved in biological uptake of inorganic substances and the controlling factors, including exposure history. Also included will be mathematical representations of uptake (if any), schemes for predictability (if identified), and comments on appropriate uses. To the extent possible, we will examine how this information can be used to understand real exposure circumstances.

4.3 Available Criteria and Data

4.3.1 Terrestrial Plants

- Irrigation standards, other (?)
- Tabulation of some data for selected contaminants

TABLE 6 (continued)

4.3.2 Aquatic Biota (fresh and saltwater)

- Freshwater fish, invertebrates, others (?)
 - selected standards (probably EPA Water Quality Criteria)
 - tabulation of data for selected contaminants
- Saltwater fish, invertebrates, others (?)
 - selected standards
 - tabulation of data for selected contaminants

Subsections 4.3.1 and 4.3.2 will include any available criteria or standards for safe levels. Data on selected contaminants will be tabulated to show known ranges of typical concentrations and ranges of problematic concentrations, emphasizing uptake-related consequences without excluding toxicity implications. Each subsection will also discuss exceptions, problem areas, and where appropriate, some general information about closely related constituents.

4.4 Models

A brief discussion of any uptake models that are identified.

4.5 Extraction Methods for Predicting Availability to Biota and Understanding Levels in Biota

A brief discussion of analytical methods used to "determine" the amount of pollutant in a matrix (e.g., soil, water) that is available for uptake. Also measurement methods used for biota.

5. Models for the Prediction of Environmental Fate

5.1 General Considerations

5.1.1 Users' Guide to Model Use

- Overview of what the chapter will do for the user
- Essential considerations and concepts for model use

5.1.2 General Functions of Models

- Chemical speciation
- Mass transfer and pathway models
- Adsorption processes
- Kinetics

TABLE 6 (continued)

5.1.3	<p>Categories of Models and Applications of Models</p> <ul style="list-style-type: none"> • State-of-the-art in modeling capabilities • Factors to consider in selecting a model • Results and output to expect from a model • Problem definition -- Choice of appropriate model(s) as a function of environmental/pollutant fate scenario
5.2	<u>Environmental/Pollutant Fate Scenarios</u>
5.2.1	Definition and Summary of Scenarios
5.2.2	<p>Land</p> <ul style="list-style-type: none"> • General • Disposal • Land treatment <ul style="list-style-type: none"> --run-off --sediment • Agricultural practices • General non-point source • Other
5.2.3	<p>Soil</p> <ul style="list-style-type: none"> • General • Land disposal • Land treatment • Storage • Injection
5.2.4	<p>Groundwater</p> <ul style="list-style-type: none"> • General • Areal • Point-source in aquifer • Interception of flowing groundwater • Other groundwater flow alteration methods
5.2.5	<p>Other Underground (not soil)</p> <ul style="list-style-type: none"> • Nuclear waste repositories
5.2.6	<p>Water</p> <ul style="list-style-type: none"> • General • Lake/pond/reservoir • Stream • Estuary • Ocean
5.2.7	<p>Air</p> <ul style="list-style-type: none"> • Dispersion models • Chemical models
5.2.8	Uptake by Biota

TABLE 6 (continued)

5.3 Models

5.3.1

Introduction

- Nature of Models
- Lineage

5.3.2

Description of Models

- Summary table and flow chart
- Individual models

EQ3

PATH1

EQ6

PHREEQE

GEOCHEM

REDEQL2

MEXAMS

SESOIL

MINEQL

SOLMNEQ

For each model selected, the following topics will be covered:

- Applicability, uses
- Availability, hardware requirements
- Description (in moderate detail)
- Data requirements
- Form and content of output
- Ease of use

5.3.3

Modelling/Calculation Issues

- Data acquisition
- Mathematical and numerical techniques
- Kinetics
- Material transfer
- Adsorption
- Speciation -- calculation of activity coefficients

5.4 Sample Problems

● PART II - THE ENVIRONMENTAL PROPERTIES OF IMPORTANT ELEMENTS, LIGANDS AND CHEMICAL CLASSES

This section will contain five major subsections, each focusing on a group of elements, ligands or chemicals of special interest. The content of each section may vary with the nature of the elements/chemicals. A matrix chart or decision tree may be used to show which generic processes/properties are important in each subsection; a cross reference to the appropriate Part I subsection will also be provided.

TABLE 6 (continued)

6. Major/Matrix Elements and Ligands

[Elements: Na, K, Ca, Mg, Si, Al, Fe]
[Ligands: OH⁻, Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻]

6.1 Properties, Speciation in Water

[Both fresh and saline waters to be covered]

6.2 Properties, Speciation in Soil

7. Trace or Pollutant Metals

[Coverage: Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag,
Tl, Zn]

For each metal, predominant inorganic species in water will be emphasized, especially ligand compounds with hydroxide, chloride, sulfate, carbonate/bicarbonate, sulfide, oxide, silicate, hydrosulfide, etc. as appropriate. Key subsections are listed below; see Sect. IV of this report for details.

7.1 Properties of the Elements

7.2 Fate Processes in Aquatic Environment

7.2.1 Fresh Water

7.2.2 Saline Water

Data on speciation, precipitation, adsorption, volatilization, etc. will be given in 7.2.1 and 7.2.2 as appropriate.

7.3 Fate Processes in Soil

8. Trace or Pollutant Ligands

8.1 Nitrogen-containing Ligands

8.2 Sulfur-containing Ligands

8.3 Phosphorus-containing Ligands

8.4 Fluoride

8.5 Bromide

Each of these subsections will briefly summarize the relevant natural cycles and will provide stability constants and other property data relating to the environmental fate of applicable structures/complexes.

9. Radionuclides

9.1 Naturally occurring

9.2 Artificial

Both subsections will provide data on radioactive properties (e.g., half-life, radiation emitted, daughters) as well as chemical/ environmental properties.

TABLE 6 (continued)

10. Chemical Classes

General discussion of properties, plus data on selected chemicals in each class (see examples in Section IV of this report).

- 10.1 Organometallics
- 10.2 Acids
- 10.3 Anionics
- 10.4 Salts
- 10.5 Oxides
- 10.6 Gases
- 10.7 S-Containing
- 10.8 P-Containing
- 10.9 Si-Containing
- 10.10 B-Containing
- 10.11 Bases (Hydroxides)
- 10.12 Carbonyls
- 10.13 Carbides
- 10.14 Cyanides
- 10.15 Hydrides
- 10.16 Hypochlorites, Chlorates
- 10.17 Peroxides
- 10.18 Selected Binary Compounds

• APPENDICES

The list below is tentative. Some portions may currently duplicate material in Part I or II of the proposed Handbook.

- A. Sources of Measured Data
- B. Natural/Background Concentrations of the Elements (and other inorganic species)
This appendix could also provide data on concentrations in "polluted" environments. Detailed scope of proposed coverage given in Section IV of this report.
- C. Description of Soil Types, Properties
- D. Pollutant Criteria or Standards

• SUBJECT INDEX

Both subjects and named chemicals will be indexed, possibly in separate lists.

IV. DISCUSSION OF HANDBOOK OUTLINE, CONTENTS, APPROACH
PART I - GENERIC DESCRIPTION OF PROCESSES AND PROPERTIES

1. Transport and Transformation Processes (Section 1)*

The first section of the inorganics handbook is designed to fulfill two basic purposes:

- Provide the Handbook user with an overview of the important transport and fate processes in each environmental compartment (air, water, soil, biota); and
- Provide a guide to subsequent sections, primarily in Part I, for the user who wishes to investigate one or more processes in further detail.

An initial overview (Section 1.1) will provide a series of diagrams, flowcharts and tables showing, for each medium, the important environmental transport and fate processes. Intercompartmental transfer processes (e.g., volatilization from water to air, dry deposition from atmosphere to land) will also be listed. One or two chemicals (e.g., a metal and a ligand) may be chosen as examples. The Handbook user, if unfamiliar with all of the transport and reaction pathways, will be able to use this section to identify general properties of interest, and will be directed to subsequent subsections (1.2 - 1.5) or other sections for further information.

Subsections 1.2 - 1.4 will focus on the processes and properties important for inorganic chemicals in a specific medium: air, water or soil. Again, diagrams and tables will be used to summarize the important properties and to cross-reference applicable sections of Parts I and II of the Handbook. Brief text descriptions of these processes will be given.

Subsection 1.3 ("Water Mediated" processes) will, for example, briefly define and describe the importance of: (1) speciation, (2) the types of reactions affecting speciation (e.g., acid-base equilibria, oxidation/reduction), (3) solubility considerations (dissolution/precipitation), (4) adsorption onto soils and sediments, (5) microbial transformations, (6) uptake by aquatic biota, and (7) other processes, as necessary. Where possible, the relative importance of processes for different types of chemicals (e.g., cations, anions, neutral species, chemical classes) will be mentioned. The section will provide specific cross references to subsequent sections where further generic descriptions (Part I) or data compilations (Part II) are provided. For example, the reader will be referred to Section 2.3.3 for a generic description of acid-base equilibria, Section 3 for a generic description of rates of acid-base reactions, Section 5 for the

* Parenthetical references key this material to the corresponding sections of the proposed Handbook as outlined in Table 6.

modeling of speciation reactions, and Section 7 for environmentally important property data, including acid-base equilibrium constants, for rare metals such as chromium, lead and mercury.

A final Section (1.5) will provide a brief overview of radioactive decay and processes of special interest with regard to the fate and transport of radionuclides in the environment.

The sections will also provide cross references to Tables in Part II of the Handbook where specific data can be found, e.g., on equilibrium constants.

2. Estimations Associated with Equilibrium Conditions

a. Introduction

As shown in the detailed outline for the Phase II Handbook (Table 6), we plan to cover about twenty properties or processes that may be associated with equilibrium conditions. The discussions below provide detailed descriptions of the proposed coverage for eight of these processes. We believe the ones selected for treatment here will adequately illustrate the manner in which we would propose to cover the others.

b. Gas Adsorption on Solids (Section 2.2.3)

The extent to which a gas is adsorbed on a solid surface is related to the rate at which that gas is released and transported to the environment. Despite the fact that, under environmental conditions, a gas has a vapor pressure greater than 1 atmosphere, some gases that are strongly adsorbed to solid surfaces may persist for some finite time on that surface before being released into the atmosphere. Thus, it is important to be able to estimate how strongly a given gas might be adsorbed on a surface, so as to ultimately determine its persistence and the rate at which it will be released to the air environment.

In general, there are two main types of adsorption, depending upon whether the association between the gas and solid surface is physical or chemical in character. The first type, known as Van der Waals adsorption, is characterized by relatively low heats of adsorption (≤ 5 kcal/mol), which are about the same order as heats of vaporization. The equilibrium between solid and gas is reversible, and is rapidly attained when the temperature and pressure are changed. Physical adsorption is usually favored at low temperature.

All gases exhibit Van der Waals adsorption, but in some cases the second type of adsorption ("chemisorption") may be favored, especially at higher temperatures. The heats of adsorption are in the range of 20 to 100 kcal/mol, indicating that chemical forces are at play.

Theoretical treatments of both types of adsorption are due to Langmuir, who derived the following relationship between the amount of gas adsorbed and the gas pressure:

$$\frac{X}{m} = \frac{K_1 K_2 P}{1 + K_1 P}$$

where X is the amount of gas adsorbed per weight, m , of solid adsorbent, K_1 and K_2 are constants and P is the partial pressure of the gas at equilibrium. The equation is based on the assumptions that equilibrium has been established between the gas and the solid and that only a monomolecular layer of gas molecules has been adsorbed. These assumptions are probably valid at environmental temperatures and

* Langmuir, I., J. Am. Chem. Soc. J, 38 2221 (1918).

pressures; it is only at very low temperatures and at pressures approaching the saturated vapor pressure of the gas that multilayer adsorption occurs.

Experimentally, the amount of gas adsorbed on a given adsorbent is determined in apparatus where the volume is known and in which the pressure and temperature can be varied and accurately recorded. Numerous systems have been commercialized for determining, via gas adsorption, the surface area of an adsorbent. Data from measurements made in such apparatus yield the amount of gas adsorbed directly.

Methods of estimating the extent of physical adsorption to be expected for a given gas have not been developed; however, we believe that there is some hope of developing a method that will at least lead to rough estimates. One possibility may be to establish correlations between adsorption coefficients and other physical properties. For example, the logarithm of the volume of gas adsorbed per gram of adsorbent varies generally in a linear fashion as a function of the normal boiling point of the gas for various organic and inorganic gases. Figure 1 illustrates this relationship with data taken from Glasstone. The data plotted were obtained at 15° C for a variety of inorganic and organic gases and exhibit a linear relationship with a correlation coefficient of 0.969.

We believe that this type of correlation can be developed into a method to estimate the relative adsorption of a given gas, which would then allow us to predict the rate at which it will be released into the atmosphere.

To a first approximation, chemisorption need not be a concern, as it usually occurs at temperatures well above ambient. In cases where it has been observed at low temperatures, the solid surface was usually a metal, and the chemisorbed gas was usually oxygen or carbon monoxide. We probably need not concern ourselves with gases boiling well below approximately 200° K, as it is obvious that they would have relatively low adsorption and hence would not persist on solid surfaces.

* Glasstone, S., Textbook of Physical Chemistry, 2nd edition, D. Van Nostrand, New York, 1946.

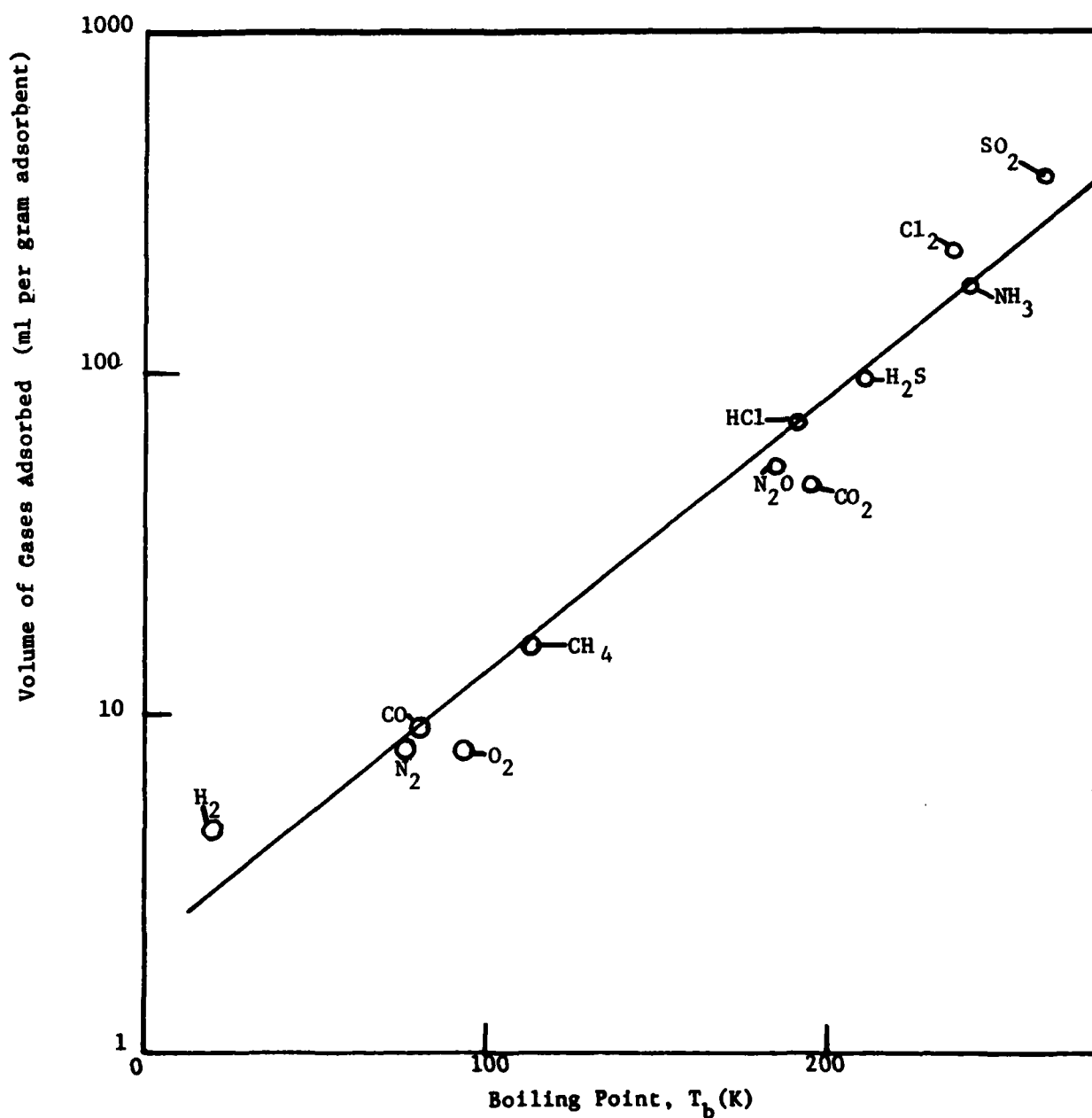


Figure 1: Adsorption of Various Gases as a Function of Normal Boiling Point (Data obtained at 15°C)

Source: Data from Glasstone, S., Textbook of Physical Chemistry, 2nd edition, D. VanNostrand, New York, 1944

c. Acid-base Equilibria and Hydrolysis (Section 2.3.3)

(1) Description of Property

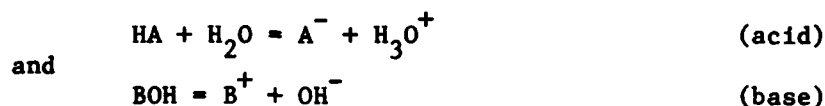
The Arrhenius definition of acid-base behavior or character is useful in considering environmental problems. According to the Arrhenius model, an acid is any hydrogen-containing compound that gives hydrogen ions in aqueous solution, and a base is any hydroxyl-containing compound that gives hydroxyl ions in aqueous solution. This concept must be extended to include species that do not contain hydrogen (e.g., CO_2) or hydroxyl (e.g., NH_3) but which react with water to liberate hydrogen or hydroxyl ions. Thus, substances that increase hydronium-ion concentration are called acids and those that increase the hydroxide-ion concentration are called bases.

When certain salts are dissolved in water, the resulting solutions are observed to become slightly acidic or slightly basic. These interactions between salts and water, which are fundamentally similar to acid-base reactions, are called hydrolysis. In principle, any negative ion can act as a base, and any positive ion that hydrolyzes generally produces acidic solutions. In practice, however, most negative ions compete only slightly with OH^- for protons, and in aqueous solutions of these ions the extent of hydrolysis is small.

Any attempt to describe the properties of metal ions in aqueous solution must consider hydrolysis reactions. Most cations undergo hydrolysis reactions in aqueous solution because (1) they form strong bonds with oxygen atoms, and (2) hydroxide ions are always present within the broad concentration range of 10^{-14} M due to the self ionization of water.

(2) Mathematical Description

For an acid HA and a base BOH, we have acid-base equilibria



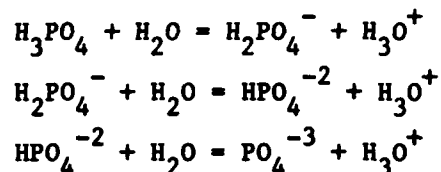
with corresponding equilibrium constants

$$K_a = \frac{(a_{\text{A}^-})(a_{\text{H}^+})}{a_{\text{HA}}} \quad \text{and} \quad K_b = \frac{(a_{\text{B}^+})(a_{\text{OH}^-})}{\text{BOH}}$$

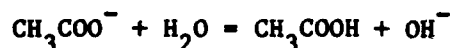
where a_i = activity of species i . Hydrolysis reactions occur with the species A^- or B^+ to produce basic or acidic changes (respectively) in an environment. For $K_w = (a_{\text{H}^+})(a_{\text{OH}^-}) \approx 10^{-14}$, we have respective hydrolysis constants of

$$K_h(A^-) = \frac{K_w}{K_a} \quad \text{and} \quad K_h(B^+) = \frac{K_w}{K_b}$$

Many species are multi-acidic or multi-basic and can dissociate to give more than one hydrogen ion or hydroxyl ion. Phosphoric acid is an example:



One of the most important applications of simultaneous equilibria is the quantitative description of hydrolysis. A weak acid and its anion are a conjugate acid-base pair. If an acid is weak, its conjugate base tends to be strong. Acetic acid, for example, is a moderately weak acid, so acetate ion is a moderately strong base and will tend to acquire protons in aqueous solution by the reaction

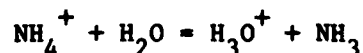


The above reaction, which is essentially just the ionization of a weak acid, represents the hydrolysis of the acetate ion. The equilibrium constant for the above reaction is

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = K_h$$

where K_h is called the hydrolysis constant. Hydrolysis constants are not often tabulated, because they can be evaluated easily from the ionization constants of the corresponding acid and the ion product constant for water. These calculations reflect the fact that hydrolysis is an aspect of acid-base equilibria.

The salts of weak bases are themselves weak acids. For example, NH_4Cl will act as a weak acid and be hydrolyzed according to



(3) Related Environmental Scenarios

Any inorganic compound with acidic or basic properties has the potential to modify pH when dissolved in solution or in contact with an aqueous environment. In some cases, and particularly when buffer

effects are insignificant, such compounds can cause local pH conditions to fall outside the range (6-8) typically encountered in the natural environment. Thus, to generate quantitative predictions of the activities of constituent species in a given environment, the existence of multiple acid-base ionization equilibria must be considered.

Further reactions of a given compound or species in the environment will depend on the form of the dissolved species. For example, the vapor pressure of a gas (e.g., CO_2) above a solution of the corresponding acid (H_2CO_3) will depend on the concentration of undissociated acid. The latter concentration will, in turn, depend on the concentrations of the acid-base equilibria species (CO_3^{2-} and HCO_3^-) and the pH of the solution. Another example is the adsorption of dissolved species onto soils. If different ionic charges are associated with the various dissolved species (e.g., Cd^{+2} , CdOH^+ , $\text{Cd}(\text{OH})_2$), each may have a different affinity for the soil adsorption sites. These aspects of chemical speciation are also very important in studies of bioaccumulation in organisms.

Hydrolysis reactions and acid-base equilibria in general are important with regard to determining the pH of an aqueous system and the chemical activity and behavior of dissolved species present in the system.

(4) Quantitative Applications in Environmental Problems

Acid or base dissociation constants can be used to calculate pH in particular systems when concentrations or activities of other species are known. They can also be used to estimate the relative concentration of various states of dissociation of a species whose total concentration is known.

An exact treatment of ionization or acid-base equilibria can require manipulation of complex equilibrium expressions and should involve considerations of material and charge balance relations. For example, to estimate the concentration of "free" Cd^{+2} ion in a solution of a particular pH and complexing ions, values of the acid dissociation constants for $\text{Cd}^{+2}/\text{CdOH}^+$ and $\text{CdOH}^+/\text{Cd}(\text{OH})_2$ are required.

(5) Estimation of Acid-Base Equilibria and Concentrations (Activities) of Inorganic Species

The following approaches to estimation of acid-base equilibria effects will be considered:

- Ionization equilibria for a simple system: We will describe the considerations and steps involved in the exact quantitative representation of acid-base and hydrolysis equilibria for a simple system. This treatment will serve as a starting point for subsequent discussion of more complicated systems.

- Multistage equilibria: In most environmental systems, the presence of two or more weak acids or bases in solution must be considered. These multiple equilibria arise naturally when, for example, an acid ionizes in two or more ways. We will describe the series of steps involved in calculating equilibrium speciation for the major components of a complex, multistage aquatic system. The ultimate mathematical treatment relies upon total concentrations of components, identification of known species, material balance and charge balance expressions, numerical values of equilibrium constants and determination of activity coefficients for key species. Buffer effects must be described in connection with multistage equilibria calculations.
- Tabulation of relevant data: A wide variety of acids (e.g., hydride acids such as HCl , oxyacids such as H_3AsO_3 , transition metal ions) and bases have been studied experimentally, and the literature contains a great deal of data on equilibrium constants. These data are valuable for estimating otherwise unknown equilibrium constants. We will tabulate such data for a selected number of environmentally important elements in common aqueous-stable forms.
- Estimation methods based on thermodynamic cycles; For species of environmental importance that cannot be estimated by the methods described above, we will evaluate the utility of estimation methods based on thermodynamic cycles. Such methods have been considered for hydrogen halide acids, potentially valuable trends have been noted, and values predicted for oxy acids.
- Estimation of trace elements: Many trace elements have not been studied thoroughly, and data for some key elements have not been collected. The constants for solution complexes that cannot be isolated and studied are required for environmental speciation and exposure calculations. We will review the literature and, if appropriate, tabulate key data for these elements. For trace elements, we will evaluate alternative concepts for estimation.
- Graphical methods: In certain instances, graphical methods are useful for defining regions of stability of various acid-base species. We will describe methods for constructing such representations and note appropriate applications.

d. Ligand Formation (Section 2.3.4)

(1) Description of Property

The chemistry of metals in solution is essentially the chemistry of their complexes. A metal ion in solution is coordinated to solvating water molecules or to other ligands. Complex formation can be viewed as the tendency and extent to which hydration spheres of a dissolved ion are modified by other ions (or ligands in general). The process can involve outer-sphere association with the ion (e.g., ion pair formation) or inner-sphere complex formation, i.e., bond formation between the central atom (usually a metal ion) and the newly associated ion.

The transition-metal ions are Lewis acids, and their complexes are quite stable. The cations of the more electropositive metals (i.e., alkali or alkaline earth metals) are weaker Lewis acids and form fewer complexes; they are hydrated in solution, but their interaction with water is much weaker than that of transition-metal ions.

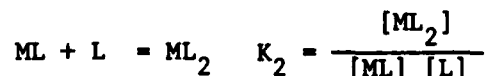
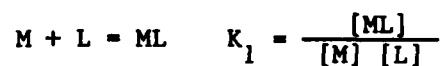
(2) Mathematical Description

The stability of a metal complex, MX_m^{n+} , is usually expressed in terms of the formation constant, β_m for the reaction:

$$M^{n+} + mX = MX_m^{n+} \quad \beta_m = \frac{[MX_m^{n+}]}{[M^{n+}] [X]^m}$$

The value β_m expresses the thermodynamic stability of the complex, since it is an equilibrium constant from which one can calculate a free-energy change for the formation of the complex.

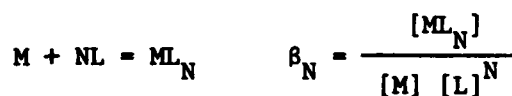
It is worthwhile to consider the constants for each step in the formation of a complex between a metal M (without specifying charge or degree of solvation) and a ligand L:



In general,



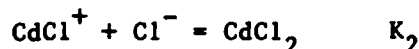
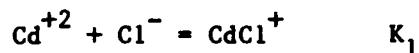
Another way of expressing the equilibrium relations is:



K_1 is called the stepwise formation constant or stability constant, and β_1 is called the overall formation or stability constant. Thus,

$$\beta_m = K_1 K_2 \text{ ---- } K_m$$

For example,



The overall stability constant for the $CdCl_2$ complex in solution is given by

$$\beta = K_1 K_2$$

(3) Related Environmental Scenarios

Inorganic substances will adapt to the particular environment to which they are exposed in solution, subject only to kinetic restraints. This environment will include many ions and ligands that can complex or form ion pairs. When complex formation occurs, chemical properties such as solubility, attenuation capacity in soils, fish bioconcentration factors and toxicity are modified. For example, the formation of chloro-complexes in seawater reduces the activity of free, uncomplexed metal ions that may have significantly greater toxicity. In this case, the altered toxicological impact may be associated with altered bioavailability as well as altered pharmacological activity. These effects underscore the importance of chemical speciation calculations in environmental pollutant analyses.

(4) Estimation of Ligand Formation Effects

- Effect of metal ions and natural orders of stability: The stabilities of complexes formed by various metals follow some regular trends, which are often related to size and charge effects. Although metals differ greatly in their tendency to form complexes with various ligands, there are some helpful trends within groups of similar metals. For example, for a variety of ligands, the divalent metals in the first transition series show an increase in formation constants from Mn^{+2} through Cu^{+2} followed by a drop at Zn^{+2} . The order $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$ is referred to as the "natural order of stability."

We will list relevant orders of stability for various categories of metal ions and summarize any explanations of them that have been suggested. Stability constants in these series will be tabulated and may also be used as a basis for estimating the stabilities of particular metal-ligand species when experimental values are not available.

- Effect of ligand atom: Several approaches have been identified for classifying the stability of complexes as a function of ligand character. For example, for the more electropositive metals the order of stability of the halide complexes is $F > Cl > Br > I$; the reverse order is observed for highly polarizing metal ions such as Hg^{+2} . Metals have also been classified according to their acceptor properties. In other instances, the increase in stability of complexes can be described in terms of increasing basicity of ligands.

We will summarize relevant orders of stability for various categories of ligands. Factors that appear to be important in establishing these trends will be described. Tabulated values of stability constants in these series will be used, as above, to summarize the stability relations and to provide a basis for estimation of stabilities when experimental values are not available.

- Taube's classification: Correlations between electronic configuration and rates of reaction of inner orbital octahedral complexes can be used, as first described by Taube, to distinguish between labile and inert complexes. We will evaluate the usefulness of extending this approach to the estimation of stability constants when experimental data are not available and as a quick means of evaluating complex stability in various environmental situations.
- Graphical methods: These can be particularly useful in analyzing multistage equilibria associated with complex formation. Multiple stability constants can be reduced to

expressions involving master species, than distribution coefficients or species molarity can be plotted as a function of pH or anion (ligand) activity. It is frequently discovered that representation of complex, multistage equilibria can be dramatically simplified with such plots; typically, for a fixed pH or ligand activity, they reveal that speciation involves just two significant components from a longer list of possible species.

We will describe how graphical methods can be employed to estimate complex formation activities, situations in which such methods are useful, and the techniques involved in constructing appropriate plots.

The literature contains useful summaries of complex formation and stability in a variety of formats (e.g., Ringbom's Complexation in Analytical Chemistry). The Atlas of Metal-Ligand Equilibria in Aqueous Solution, by J. Kragten, contains plots for 45 metals and 29 ligands under a variety of conditions. Applicable criteria and methods for using such plots will be described.

e. Electron Transfer: Oxidation/Reduction (Section 2.3.5)

(1) Description of Property

Chemical reactions in which one or more electrons are actually transferred from one species to another constitute a major domain of electrochemistry, namely, homogeneous oxidation/reduction reactions. Redox processes are an important class of reactions in natural waters. In these reactions, species that give up electrons are oxidized, and species that acquire electrons are reduced.

Redox potentials affect the stability and occurrence of electroactive materials (atoms, molecules and ions) in solution. Some redox couples can dominate the redox potential of solutions in the same way that certain strong acids can control the pH of a solution. Other species respond to the potential of the environment, and are speciated according to the redox characteristics of the environment.

Both the standard-state potential and the activity coefficients of dissolved species are of fundamental importance to the thermodynamic properties of electrolyte solutions. Standard state potentials have been tabulated for hundreds of redox systems, and methods of varying utility are available either to calculate or to measure species activities.

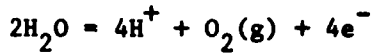
(2) Mathematical Representation: E, Eh, pe

In general,

$$E = E^\circ_{\text{redox}} - \frac{RT}{nF} \ln \frac{(\text{oxid})}{(\text{red})}$$

where (oxid) is the activity of the oxidized species and (red) is the activity of the reduced species.

A parameter Eh is defined as the emf, E, relative to the standard hydrogen reference electrode. The Eh of water is often controlled by the reaction



for which

$$\text{Eh} = 1.23\text{V} = 0.0592 \text{ pH} + 0.0148 \text{ pO}_2$$

Eh expressions can be derived easily for aerobic water (considered in preceding paragraph), anaerobic or anoxic waters, oceanic waters and also for waters in contact with one or more solid phases. In practice, Eh is difficult to measure in aerobic waters due to competing reactions, especially involving peroxide. A meaningful quantity is relatively easy to obtain for anoxic waters.

The quantity pe is a convenient representation of Eh, to which it is related by

$$pe = \frac{F}{2.3 RT} Eh$$

so that $pe = -\log(e^-)$

where pe represents a relative activity of electrons, in a similar sense to that in which (H^+) in $pH = -\log(H^+)$ represents the relative activity of protons.

(3) Related Environmental Scenarios

Although it can be difficult to measure the Eh in aerobic waters, values derived from calculations, estimates or direct measurements (when possible) can be used to calculate distributions and activities of redox species with the help of Eh - pH diagrams.

The Eh value in a system can be controlled by certain redox couples when the oxidized and reduced species of the couple are present as major constituents of equilibrium systems at given values of pH . On the other hand, couples that are minor constituents of an environmental system respond to the Eh imposed on them and can be used as Eh indicators under certain conditions.

An Eh - pH set of data can be used in anoxic water to determine mineral assemblages at equilibrium. Under these conditions, Eh is often fixed by bacterial reduction of SO_4^{2-} (to H_2S , HS^- and S^{2-}), and heavy metal concentrations are controlled in large part by the solubilities of their metal sulfides.

While the true Eh cannot be calculated theoretically for oxygenated waters when slow biological reactions occur, it can be calculated for sterile oxygenated waters and then utilized to calculate activities of environmentally important redox species.

(4) Quantitative Applications in Environmental Problems

Redox Eh or pe values, often in combination with pH data, can be used to define quantitatively the activities of environmentally important redox species. Eh - pH and pe - pH diagrams can be used to estimate the stability range of various substances. The decision regarding whether an oxidizing or reducing agent is stable in solution should be made on the basis of Eh .

Eh values vary with each environment and among environments to a much greater extent than does pH , partly because of their interactions with biota. A distribution (i.e., a two-dimensional graphical representation) of Eh - pH values in different environments can be used to differentiate easily between environments such as rainwater, shallow marine sediments, denitrifying bacteria, open sea sediments or sulfate-reducing bacteria.

(5) Estimation of Environmental Quantities Based on Redox Properties and Measurements

The following approaches to estimation methods based on redox properties will be considered:

- Definition of redox quantities: We will describe and define the parameters that are useful in considering redox equilibria and in estimating activities of environmentally important redox species. The role of activities, ion pair and complex formation, pH, Eh and pe will be defined more rigorously, and the limitations of each of these parameters in environmental analyses will be summarized.
- Applicability of redox measurements: As described briefly in the foregoing paragraphs, measurements or calculations of parameters such as Eh can be very useful in certain environments and spurious in others. The regimes in which various redox parameters can be used, calculated or measured will be described in more detail.
- Approaches to estimation in various systems: The conceptual breakdown or division of systems of environmental interest will be described. The important equations and relevant calculations will be elaborated for a simple redox equilibrium, aerobic and anaerobic systems, oceanic waters, systems in equilibrium with one or more solid phases, and mineral assemblages.
- Eh-pH and pe-pH diagrams and calculations: We will describe methods by which Eh-pH and pe-pH diagrams can be constructed and explain how and when they can be used to estimate the stability fields and activities of various species. This information will indicate the ranges of Eh and pH in which given substances are stable in contact with aqueous solutions.
- Ranges of environmental values: We will describe the ranges of Eh and pH that are encountered in various environmental systems, and we will examine the degree to which these parameters are specific for particular environmental scenarios.
- Other diagrams of importance: The activities of important species can sometimes be fully defined by plotting parameters other than Eh-pH or pe-pH. Of course, these other diagrams include acid-base multi-equilibria and complex formation stability regions. In the context of redox quantities, Eh-pCO₂ diagrams (for example) can be employed to estimate redox species that involve carbonate compounds (e.g., iron mineral systems).

- Use of models to consider redox equilibria: The extent to which computer-encoded models can be used to describe complex redox equilibria will be discussed. We will refer the potential user to those specific models that may be worth considering and to the portions of Section 5 of the Handbook that describe their use.
- Non-equilibrium considerations: We will describe the mathematical techniques that can be used to predict (eventual) redox equilibrium conditions when the system is not at equilibrium. We will also describe briefly the limitations of redox calculations, which are thermodynamic, in predicting equilibrium situations that may not be achieved due to kinetic limitations.

f. Adsorption/Uptake

(1) Description of Property

A major challenge facing environmental chemists, and aquatic chemists in particular, is to account quantitatively for chemical processes that occur at solid-liquid interfaces. Atoms, ions and molecules located "near" surfaces are subjected to unbalanced chemical forces. Adsorption, whether chemical or physical, is a process by which the system as a whole responds to this imbalance by creating a more stable chemistry in the interfacial region.

Adsorption from solution onto the surface of a solid can involve removal of solute atoms, ions or molecules from the solution, and can also involve exchange reactions of the solution with the solid surface. Two main types of adsorption can be clearly distinguished. In physical adsorption, the forces creating adsorbed species are of a physical nature and are relatively weak (compared with normal bond energies); these van der Waals or electrostatic attraction forces play only a minor role in affecting the reactivity of adsorbed molecules. In chemical adsorption (chemisorption), adsorbed particles are held to the surface by much stronger forces; the net energy of interaction with the surface results from short-range chemical forces such as covalent bonding, hydrophobic bonding, hydrogen bridges, and steric or orientation effects. The Handbook will summarize the important characteristics of physical and chemical adsorption.

Experience has shown that the equilibrium distribution of adsorbate species between the surface of an adsorbent and the liquid phase depends upon temperature, solute concentration, nature and area of the adsorbent, and the nature of the adsorbate and solvent. An adsorption isotherm, which relates the quantity of adsorbed material to the adsorbate concentration in solution at constant temperature, is by far the most convenient method of defining an experimentally determined adsorption equilibrium.

(2) Mathematical Representation

Early modeling of adsorption phenomena has involved describing the partitioning of an ion or molecule between solid and liquid phases. Simple models of adsorption such as the Freundlich and Langmuir equations* have been used successfully to account for adsorption phenomena. In practice, these models have been found useful for quantitatively describing the adsorption process -- that is, they have an empirical basis. The Langmuir isotherm and corresponding model assume ideal behavior, which is overly simplistic for environmental applications. Also, mathematical descriptions of adsorption have no explicit dependence on pH, ionic strength, electrostatic environment, surface species interactions or surface precipitation.

* Stumm, W. and J. J. Morgan, Aquatic Chemistry, 2nd ed., John Wiley & Sons, Inc., New York, 1981 (p. 605 ff).

The Temkin isotherm (sometimes referred to as the Slygin-Frumkin isotherm), which we will describe in the Handbook, has recently been successful in using expressions for energetics of lateral interactions between adsorbate particles to modify heats of adsorption as a function of surface coverage. In its simplest form, this model assumes that the decrease in heat of adsorption with increasing coverage is linear; the Freundlich isotherm, in comparison, assumes a logarithmic decrease.

The Freundlich and Langmuir isotherms are most frequently used to represent experimental data on adsorption from solution. The Freundlich equation has the form:

$$x = k c^{1/n}$$

where c is the concentration of adsorbate in solution at equilibrium, x is the amount adsorbed and k and $1/n$ are constants. The equation is frequently used in the form which is simpler for plotting experimental

$$\log x = \log k + \frac{1}{n} \log c$$

data and estimating the constants. The Freundlich equation, in this format, successfully represents adsorption phenomena in a wide variety of systems. However, it does not express the adsorbed quantity (x) as a linear function of c at low concentrations, as is commonly observed experimentally. Also, since there is no provision for a maximum value of x , the equation predicts infinite surface coverage at infinite concentration. Accordingly, the application of the Freundlich isotherm is limited to intermediate ranges of surface coverage.

The process of adsorption from solution is more difficult to treat theoretically than the corresponding gas-on-solid process. The Freundlich isotherm can be applied to the adsorption of gases, but has been used principally for adsorption from solutions. Experimental results conform to the Freundlich isotherm when a plot of $\log x$ vs $\log c$ yields a straight line.

The Langmuir model predicts that under equilibrium conditions and constant temperature, adsorption conforms to an isotherm of the form:

$$x = \frac{x_m c}{k+c}$$

* Slygin, A. and A. Frumkin, *Acta Phys.-Chim. URSS*, 3,791 (1935); and: Temkin, M.I. and V. Pyzhev, *Acta Phys.-Chim. URSS* 12:327 (1940).

where x_m is the amount needed to form a monolayer. Although developed for gas^m adsorption, the simple Langmuir equation is often used to describe adsorption from solution by heterogeneous solids. The model is derived from some assumptions that are ideal -- namely, that there is no interaction between adsorbed particles (i.e., the heat of adsorption is independent of coverage), that all surface states possess the same adsorption energetics (i.e., no active sites), and that adsorption is proportional to adsorbent concentration.

When multilayer adsorption is expected, the BET isotherm (due to Brunauer, Emmett and Teller) can successfully model the process. The theory is based on assumptions similar to those used to derive the Langmuir equation, except that multilayer adsorption without lateral interactions is postulated.

(3) Related Environmental Scenarios

Soil is an exceedingly complex system composed of solid, liquid and gaseous phases; it possesses organic and inorganic constituents and inert and active compounds. However, despite the wide variations in soil properties that can be encountered on a very local level, its properties can be adequately considered on a statistical basis. In soils, for example, the pH and ionic strength are usually constant. In such systems, models more elegant or elaborate than the Freundlich or Langmuir equations are not necessary.

In more complicated systems, where simple models of adsorption processes are of limited use, a common approach is to partition the surface and adsorption process into many compartments, each amenable to mathematical representation, and then to perform a statistical analysis. Variable partition (adsorption) coefficients have been used to describe alteration of the electrostatic environment at the surface, but the latter process cannot be differentiated mathematically from the effects of surface precipitation. Modeling of adsorption of ions at solid-liquid interfaces has progressed from simple empirical descriptions of adsorption as a function of adsorbate concentration to a sophisticated treatment based on thermodynamic or statistical mechanical principles that describe the process as a function of concentration, pH and ionic strength.

The long-standing and more recent isotherms are of real interest to environmental chemists because they can be used to quantify adsorption of reactive or toxic solutes and solvents by soils. The problems associated with understanding and modeling the soil-water complex must be considered in terms of the convective-dispersive transport of solutes through soil (a porous medium) and the physical or chemical

* Brunauer, S., P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60:309 (1938)

transformations of a solute during transport. The Handbook will describe environmental scenarios in which it is especially important to consider the role of adsorption/uptake processes.

(4) Quantitative Applications in Environmental Problems

Quantitative assessments of the environmental effects of adsorption phenomena involve the selection and use of appropriate adsorption isotherms. The Handbook will describe environmental scenarios in which quantitative evaluation of adsorption/uptake processes is especially important. The quantitative effects of kinetic control of adsorption processes will be described. The key equilibrium and kinetic adsorption isotherms will be described, and examples of the impact of adsorption processes in several environmental scenarios will be presented. In addition, methods to model convective-dispersive transport of adsorbed species through soil and the physical/chemical transformations of solutes will also be summarized.

(5) Estimation of Environmental Quantities Based on Adsorption/Uptake

The previous paragraphs have included a description of several of the key issues associated with quantitative estimation of adsorption/uptake processes in the environment, which will be covered in the inorganics Handbook. In addition, the following topics will be considered in connection with various approaches to estimating adsorption effects:

- The transport of a reactive solute through soil is dependent on the rate of adsorptive-desorptive reaction between the soil solution and the solid phase. In general, this process can be kinetically important whenever the relative amount of solute in a soil solution and in the soil (interfacial) matrix is changing with time, or it can be an equilibrium situation when the rate of adsorption/desorption between the soil solution and the solid phase is much greater than the rate of change in solute concentration in the soil solution due to any other cause. The Handbook will describe the implications of kinetic control of these in the environment. It will also describe and classify adsorption processes according to whether they are "slow" and kinetic factors must be considered (e.g., anion adsorption on clays).
- Several adsorption isotherms are available, or are the subject of active research, to describe adsorption processes. These isotherms are equilibrium or kinetic models. In addition to the previously indicated treatment of some selected isotherms, the Handbook will classify, describe and comment on the applicability of several equilibrium models (linear, Freundlich, Langmuir, two-surface Langmuir and competitive Langmuir) and kinetic models (reversible linear, reversible nonlinear, kinetic product, bilinear, mass transfer, Fava and Eyring, two-site kinetic and Elovich).

- Our initial evaluation indicates that the Elovich equation may have special application for describing the kinetics of heterogeneous reactions. Tentatively, it is planned for the Handbook to describe the application and derivation of the Elovich equation and its modification for nonuniform surfaces.
- The relative importance of several environmental adsorption phenomena will be considered in conjunction with an evaluation of the degree of success achieved in present understanding and modeling of these processes. The Handbook will then describe the most important selected processes and models. We expect to consider processes such as surface complex formation at oxide-water interfaces, anion adsorption at aqueous solution/mineral interfaces, cation adsorption, physical transport of adsorbed species, ion exchange processes, ionic species adsorption by hydrous metal oxides and clays, surface complexation processes, chemical speciation in the interfacial region, and adsorption coagulation.
- Elemental speciation can have profound effects on the extent of adsorption and the transport properties of adsorbed materials. Certain chemical species will saturate at specific chemical concentrations, whereas related chemical species will adsorb linearly with concentration. The Handbook will describe the effects of redox state, ligand characteristics and speciation (including degree of protonation) in determining the extent of ionic adsorption and in influencing the selection of adsorption models.
- Although several models seem capable of explaining the adsorption of cations and anions, the quantitative aspects of (for example) anion adsorption are not well understood. The Handbook will evaluate the quantitative success of some of the principal models.
- Adsorption characteristics of key classes or subdivisions of environmental adsorbents will be summarized. For example, it will be possible to summarize adsorbent properties of classes such as common soil minerals, clays, or sediment types.

g. Volatilization (Section 2.4.2)

The evaporative loss of a chemical, or volatilization, is an important source of the material contained in the atmosphere and may lead to the distribution of a chemical over areas far removed from the point of release. The process depends upon the vapor pressure of the chemical and on those environmental conditions that influence diffusion from a surface. Thus, vapor pressure is considered one of the most important parameters needed to determine the environmental fate of a chemical.

Vapor pressure values indicate the tendency of pure materials to vaporize in an unperturbed situation. For example, vapor pressure data combined with solubility or, more precisely, activity coefficient data permit the calculation of evaporation rates of dissolved species from water using Henry's Law constants.

Experimentally, vapor pressures are determined by a number of methods, depending upon the range of interest. For materials with low vapor pressure (10^{-1} mm to 10^{-7} mm), the gas saturation method is widely used. Details of this method are described in the literature.

The vapor pressures of organic materials are readily amenable to estimation. We are confident that some of the same techniques are applicable to inorganic and organometallic chemicals.

A successful estimation method requires accurate knowledge of the relationship between the heat of vaporization ΔH_v , the temperature T and the structure of the material of interest. One generally starts with the Clausius-Clapeyron equation:

$$\frac{d \ln P}{dT} = -\frac{\Delta H_v}{RT^2}$$

where P = vapor pressure (mm Hg)
 ΔH_v = heat of vaporization (cal/mol)
 T = temperature (K)
 R = gas constant (1.987 cal/mol-K)

For organic chemicals, Grain^{*} has described a method of relating ΔH_v to both temperature and molecular structure, such that the integrated form of the above equation yields a correlation that permits estimation of the vapor pressures of both liquids and solids with errors ranging from a low of 6% ($P > 10$ mm) to 20% ($P \leq 10^{-6}$ mm). The method has been verified for a wide variety of molecular structures.

* Grain, C.F., "Vapor Pressure", in Handbook of Chemical Property Estimation Methods, W. Lyman, W. Reehl and D. Rosenblatt (eds.), McGraw-Hill Co., New York, 1982.

For inorganic materials, we believe that the method described by Grain is valid and that what will be required is the determination of values for some structural parameters, particularly for organometallic chemicals.

This section will also include general discussions of vapor pressure estimation methods used by other workers and specific correlations which treat both liquids and solids.

h. Radioactive Processes and Properties

Radioactive decay is a process that can affect both the transport and transformation of materials in the environment. It occurs entirely spontaneously and is independent of all external physical and chemical influence. In general, the effects produced are so small or so rarely encountered as to be essentially of academic interest. For those rare occurrences that do have practical significance, a brief description of the unique properties and processes involved seems warranted.

(1) Recoil Transport

Radioactive decay processes involve a spontaneous loss of energy from the nucleus of the atom, which can occur in a number of different ways. In most instances the process involves the loss of an energetic electron (a beta-ray) from the nucleus, accompanied by one or more photons of gamma-radiation; more rarely, an alpha-particle, consisting of two neutrons and two protons, is emitted; and in a very few cases involving heavy elements in the transuranic series, spontaneous fission occurs, yielding two quite massive fragments of roughly equal mass. Other modes of decay include positron emission and K electron capture.

In the cases of alpha emission and spontaneous fission, the emitted fragment imparts enough kinetic energy to the remaining nucleus to cause significant recoil motion. Atoms of heavy elements that undergo alpha decay are typically transported in recoil for distances of 0.1 to 0.2 mm in air at atmospheric pressure. Atoms lying near an interface between, for instance, a host mineral and a gaseous or liquid environment such as air or water may be transported far enough by recoil to allow them to escape from one medium in which they may be relatively immobile to another in which their mobility is much greater. In the special case of multiple sequential decay, such as is found in naturally occurring thorium and uranium isotopes, the recoiling nucleus may also be radioactive and therefore hazardous to the environment.

An example of recoil transport that can lead to an exacerbated environmental hazard is that of 222-radon. When this isotope is formed by the alpha-decay of 226-radium that is occluded in mineral grains, it can be moved into an adjacent medium such as air or water. This effect has been suggested as the cause of anomalously high radon emanation from soils and minerals.

Another mechanism that can produce physical transport as a result of recoil from radioactive decay is that of spallation, the transport of neighboring atoms from a solid surface into an adjacent vapor phase. This effect has had significant implications for environmental pollution in the case of 210-polonium, an alpha-emitting isotope that occurs in nature primarily as a sequential decay product of 226-radium. When fabricated into metallic films for industrial

purposes, ^{210}Po becomes unstable with respect to spontaneous migration through the air, leading to severe contamination of nearby surfaces. Other alpha-emitters that can be produced in high concentrations and that have relatively short half-lives, leading to high "specific activity" (i.e., decay rate per gram), may also exhibit spallation transport and associated phenomena.

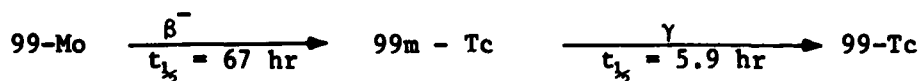
Isotopes that undergo spontaneous fission are susceptible to recoil transport, just as alpha-emitters are. Moreover, as the recoil energies of fission fragments are greater and the residual nuclei smaller, the transport ranges are generally larger.

The transport of materials caused by the recoil energy associated with certain types of radioactive decay is a subject that has received rather limited experimental treatment and is represented by a correspondingly limited literature. The process can be modeled by application of well-established physical data such as the mass of the atoms, the interatomic distances in various media, and the energies and masses of the emitted particles. Such models exist, but their experimental verification has been difficult and elusive in practice. Because the process has some practical relevance, especially in the case of the release of ^{222}Rn to the atmosphere and to groundwater, the available theoretical and experimental evidence for recoil transport associated with alpha-decay of the "uranium series" will be collected, examined and summarized. The literature will be checked to determine the validity of our present assumption--namely, that this group of naturally occurring radionuclides is the only environmentally important example of such physical transport.

(2) Elemental Transmutation

An almost universal consequence of radioactive decay, and one that always accompanies decay by beta, alpha and positron emissions as well as K-electron capture and spontaneous fission, is the formation of one or more atoms of a different element. (Alpha-particles themselves become helium atoms.) In most instances of radioactive decay, the elemental transmutation is of little or no consequence in environmental considerations, because (a) the products of most radioactive decay processes are stable (i.e., non-radioactive) atoms, and (2) they are usually produced in very small quantities and/or at extreme dilution in other media, and are therefore unlikely to be chemically significant.

In cases involving multiple sequential decay, however, at least one product will be radioactive and therefore potentially hazardous. Because this intermediate decay product is usually chemically different from its parent, it will probably behave somewhat differently in an environmental context. For example, consider composite solid waste containing an isotope such as ^{99}Tc ; the latter decays with a 67-hour half-life to form $^{99\text{m}}\text{Tc}$, a metastable isotope with a 5.9-hour half-life, that gradually decays (through isomeric transition and gamma emission) to long-lived ^{99}Tc :



This process results in a mixture whose composition varies as the parent species is depleted and its progeny accumulate. The composition can also be changed by selective chemical leaching, which can favor the technetium over the molybdenum or vice-versa, depending on the chemical form of each element.

Another familiar example of multiple sequential decay, leading to the production of species that have very different physical and chemical properties, can be found in the natural decay schemes that begin with either a uranium isotope or a thorium isotope and end, after many successive decay processes, with a stable isotope of lead, having passed first through nine or ten other elemental identities. These transient elements range from a variety of metallic species to the rare gas radon; they therefore display a wide range of behavior in the environment and have an equally wide range of significance to human health. Their environmental behavior is primarily a function of their chemical and physical properties, while their toxicity is due primarily to their radioactivity.

The result of any radioactive decay (or decay series) is usually a stable nucleus, and the residual atom, once its initial ionic charge has been neutralized, exhibits no further radioactivity or chemical activity. (Initially, atoms that have just undergone radioactive decay are likely to exhibit unusually high chemical reactivity, but unless they are highly concentrated and have high specific radioactivity, this "hot-atom" chemical behavior is not usually discernible.)

Radioactive decay that is limited to a simple transmutation results in the gradual conversion of the initial species to the product species. The rate of transformation follows an exponential law, being an entirely probabilistic phenomenon. For a large initial population of atoms of a given nuclide, the decay rate is given by the expression $N = N_0 e^{-\lambda t}$, where N_0 is the initial number of atoms, N is the number remaining unchanged after a time t , and λ is a constant characteristic of that particular nuclide species. This, of course, is similar to the rate law for any monomolecular reaction. A convenient way of expressing the decay constant λ for a given species is to show it as the time required for any given (large) number of atoms to be reduced to half its initial number by decay. Thus, for $t = t_{1/2}$, $N = N_0/2$, and $t_{1/2} = \ln 2 / \lambda = 0.693 / \lambda$.

Elemental transformation, which is frequently accompanied by corresponding chemical changes related to the change in chemical properties of the transformed nuclide, is a subject worthy of further

development, particularly for cases of sequential decay in which the newly formed species are of concern because of their hazardous radioactivity. The mathematical principles that govern the rates of formation of new species, and the quantities formed, are well known and can be summarized with appropriate examples. Values for decay constants for members of successive-decay-chain nuclides are well established and available in the literature. Examples of those that are likely to be encountered in practice can be worked out in detail, following the well-known publications of R.D. Evans et al. on the growth and decay of the short-lived daughter products of ^{222}Rn .

The extremely small mass-concentrations in which radioactive decay products are likely to occur in the environment call for special attention, in that the chemical and physical behavior of the decay products at those concentrations is likely to exhibit marked anomalies compared with those of chemically important environmental constituents. Much of this behavior can be predicted only in rather general terms, based on present knowledge, but there is a growing body of published experimental and theoretical evidence on the behavior of materials dispersed at extreme dilutions in various media and at interfaces. To the extent that this knowledge applies to radioactive decay products that either occur in nature or result from human activity, we believe that it should be included in an extended discussion of property modification associated with radioactive decay and elemental transmutation.

(3) Sequential Decay

Radioactive decay differs from most chemical reactions, in that only a single atom is involved in the energy-releasing transformation. In contrast to the interaction of two or more atoms in a chemical process, the concept of equilibrium in the chemical sense is not strictly applicable. Atoms are converted into atoms of different elements, accompanied only by loss of energy and, in some instances, matter. The term "equilibrium," when used to describe radioactive decay, implies a special steady-state condition applicable to the relative abundances of isotopes in a sequential decay process involving two or more radioactive species.

Thus, if a radioactive parent gives rise to a product species (traditionally referred to as a "daughter") that is itself radioactive and has a half-life shorter than that of the parent, a kind of constant proportionality or radioactive equilibrium eventually becomes established between the parent and daughter species, such that the ratio of the numbers of atoms of the two species is constant. During this "transient equilibrium," the decay rate of the daughter appears to be identical with that of the parent. Of course, if the supply of new daughter atoms is cut off by physical removal (e.g., chemical separation) of the parent, the true decay rate of the daughter is immediately seen.

A practical example of radioactive equilibrium is found in the system that produces the widely used medical radio-tracer, ^{99m}Tc from the decay of a longer-lived parent, ^{99}Mo . The 5.9-hour half-life metastable technetium isotope (^{99m}Tc) is allowed to grow into radioactive equilibrium with the 67-hour half-life molybdenum isotope, a process that requires about five times the half-life of the product to exceed 95% of its maximum potential, after which the desired technetium tracer is then extracted, free of the parent molybdenum, by an ion-exchange process. The process of re-supply of daughter atoms goes on constantly, governed only by the remaining supply of parent atoms, which ultimately are depleted to a level that is not practically useful. Meanwhile, the daughter-atoms can be repeatedly "milked" from the mixture.

When the half-life of a parent in a sequential decay process is so long that the activity of that species does not decrease measurably over some period of interest, and the half life of the daughter is quite short by comparison, a limiting case of radioactive equilibrium is approached, which is known as "secular equilibrium". In nature, undisturbed deposits of uranium or thorium occurring in the earth exhibit this type of equilibrium, in which the supply of some 10 or 20 isotopic species coexist in quantities determined nominally by the supply and half-life of the initial long-lived parent. For instance, ^{238}U with a half-life of 4.5×10^9 years, is the source of some 17 shorter-lived sequential daughter products, including ^{226}Ra (half-life 1590 years) and ^{222}Rn (half-life 3.8 days), culminating eventually in the stable isotope, ^{206}Pb .

If nothing disturbs such a mixture, the relative abundances of all the radioactive daughter species will remain constant, determined by that of the initial parent and limited in time by the respective half-life of each daughter product, and the "activity" or apparent decay rate of each one will be identical to every other in the series. Of course, in such a varied assortment of chemically and physically distinct elements, exposed to a variety of conditions and events in the very long period between the first decay and the rest in the series, disturbance of the mixture is probably more often the rule than the exception. The escape of gaseous radon from the earth into the atmosphere, with consequent deposit of some of its own toxic decay products in plants, animals, and humans, is an extreme example of such a disturbance, and one that creates an environmental control problem of much concern.

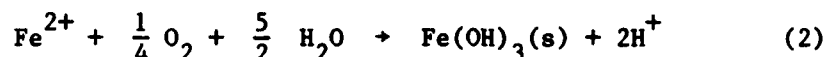
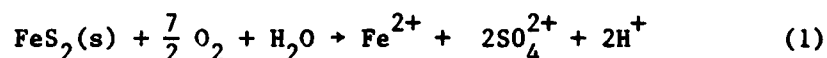
To complete the discussion of radioactive equilibrium, the case of "no equilibrium" is perhaps worth noting. The general condition of "transient equilibrium" and its special limiting condition of "secular equilibrium" have already been described as consequences of sequential decay processes in which a parent species gives rise to one or more products whose half-lives are shorter than that of the initial parent. If a radioactive daughter is produced whose half-life is longer than that of the original parent, no constant ratio ever exists between their relative abundances. This condition of "no equilibrium" is similar to that of a one-time decay in which the product has an infinitely long half-life, i.e., it is stable.

1. Microbial Transformation of Inorganic Pollutants

Knowledge of microbial transformation of inorganics, such as heavy metals, in the natural environment is rudimentary. It is known that the rate of transformation depends on environmental conditions (e.g., aerobic, anaerobic, pH, microbial population). Fungi, yeasts, algae, and bacteria all perform various steps in the biotransformation process that can affect the mobility and toxicity of inorganics in the environment.

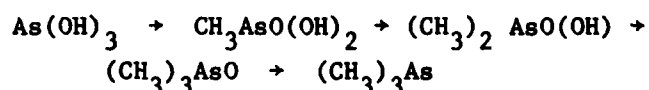
Examples of microbial transformation in nature include the following:

- (1) Oxidation: When the mining of coal exposes pyrite (FeS_2) to oxygen, a combination of autooxidation and biologically mediated oxidation (associated with microbially infested metal sulfide minerals) will produce large amounts of acid:



The second step shown above, the actual oxidation of Fe^{2+} to Fe^{3+} , is assisted by certain microorganisms. At pH 4.5-3.5 the action of the iron-rich bacteria is catalyzed, and as the pH drops below 3.5, acidophilic bacteria (thiobacillus) take over the reaction. At this stage, the rate of microbially catalyzed oxidation becomes several hundred times greater. This reaction starts spontaneously, but microorganisms have a decisive role in the maintenance and direction of the reaction.

- (2) Reduction of Nitrates: Nitrate is microbially reduced to nitrite in anaerobic soils, sediments, and aquatic environments. Further reduction of nitrite in anaerobic soils and sediments leads to NO , N_2O , or elemental nitrogen.
- (3) Microbial Methylation: Microorganisms are capable of transferring methyl groups onto various metalloids and heavy metals such as selenium, arsenic, mercury, and lead. The biological methylation of arsenic, for example, involves the following steps:



This microbial interaction results in the mobilization and potentiation of such elements as environmental toxicants. Inorganic mercury wastes may be methylated by microorganisms

in soil and add to the contamination as methyl mercury. The distinction between biological methylation and direct methylation is unclear. The methylation of mercury and other heavy metals is mediated by the same compound that is responsible for anaerobic generation of methane - methyl vitamin B₁₂. The biologic methylation of mercury occurs in anaerobic sediments.

It is known that inorganic chemicals, particularly heavy metals, can be microbially transformed in nature. These transformations may include oxidation (example 1), reduction (example 2), methylation (example 3), and presumably other reactions involving the addition or subtraction of ligands. Microbiota such as Thiobacillus and Scopulariopsis brevicalilis are capable of transforming mercury and arsenic, respectively. The rate of a microbial transformation will change depending on pH, aerobic or anaerobic conditions, and the population of microorganisms. In addition to mercury and arsenic, reductive transformation of other inorganic compounds include selenium, tin, cobalt, and thallium.

This section of the Phase II Handbook will describe the environmental settings and scenarios in which microbial transformations may be important. It will provide detailed examples for one or more of the important heavy metals (As, Hg, Pb and Se), and it will provide general guidance to the user on how to assess the likely importance (and end products) of microbial transformations for other inorganic species and other environmental scenarios.

3. Estimations Associated with Process Kinetics

a. Description of Property. Chemists are concerned with chemical systems at equilibrium, as well as with the nature and properties of chemical compounds. Section 2 described estimation methods for processes and properties of concern to the environmental chemist. An important aspect of chemistry, and the subject of Section 3, involves the study of the rates and mechanisms by which chemical systems approach equilibrium states. The acquisition of data pertaining to the rates of chemical reactions and describing the concentration dependence of reaction rate is known as chemical kinetics.

The sequence of reaction steps for a particular overall reaction is the mechanism of the reaction. In general, environmental chemists are interested in mechanisms of inorganic reactions because of the range of intermediates (of various lifetimes) that may be produced. In estimating the kinetics of reactions, knowledge of likely reaction mechanisms for categories of chemical species can frequently be used to estimate the relative rate at which a reaction proceeds.

A great variety of chemical reactions are known, and correspondingly great range of reaction times, from the apparently instantaneous to the imperceptibly slow, have been observed for these reactions. Apart from the effects of reactant concentration on overall rate of reaction, the intrinsic speed of a reaction is summarized in the rate constant.

Many chemical reactions are important to environmental chemists. We will describe estimation procedures related to chemical reactions in general. However, the majority of reactions and species of environmental interest involve complexes, and most reactions which are not instantaneous are in this class. Accordingly, much of our treatment will concentrate on the kinetics and mechanisms of reactions of complex ions.

b. Mathematical Representation. The rate of a chemical reaction is usually expressed in terms of the decrease in the amount of one of the reactants as a function of time. The rate of a reaction, always considered to be a positive quantity, is generally a function of concentrations and temperature.

For the reaction



the rate is written

$$\text{Rate} = - \frac{1}{a} \frac{dA}{dt} = - \frac{1}{b} \frac{dB}{dt} = \frac{1}{c} \frac{dC}{dt} = \frac{1}{d} \frac{dD}{dt}$$

Many reactions have rates that are proportional to the concentration of one or two of the reactants, with each reactant concentration raised to a small integral power. For reactions in which A and B represent possible reactants, the rate equations for reactions with this type of concentration dependence have the form

$$\text{Rate} = k[A] \quad (\text{termed "first order"})$$

or

$$\text{Rate} = k[A]^2 \quad \text{or} \quad k[A][B] \quad (\text{termed "second order"})$$

Reactions that proceed according to such simple rate equations are said to be reactions of the first or second order. Not all reactions have such simple rate expressions; some involve concentration terms raised to nonintegral powers, and others consist of more elaborate algebraic expressions. However, enough reactions roughly conform to simple first- or second-order rate equations to make the idea of the order of a reaction useful. It should be emphasized that the rate equation has no necessary relation to the form of the equation for the overall reaction.

A first-order reaction rate constant has units of the reciprocal of time, i.e., reciprocal seconds, and is independent of concentration. The second-order rate constant, in contrast, has units such as liter mol⁻¹ s⁻¹. The units of the rate constants for more complicated rate equations must be determined from the experimental rate expression.

Experimental results obtained from reaction rate studies are usually expressed in terms of concentration (or some quantity related to concentration) measured at various times. Experimental data are most usefully considered in terms of integrated rate expressions: e.g., for a first-order reaction with initial concentration C_0 at time $t = 0$,

$$-\frac{dc}{dt} = kc$$

Thus

$$-\frac{dc}{c} = k dt$$

Integration gives

$$-\int_{C_0}^c \frac{dc}{c} = k \int_{t=0}^t dt$$

$$\text{so that } -\ln \frac{c}{C_0} = \ln \frac{C_0}{c} = kt$$

$$\text{or} \quad \log c = - \frac{k}{2.3} t + \log c_0$$

The derived equation indicates that a first-order reaction has a linear plot of $\log c$ vs t . The use of such integrated forms of the rate expressions is usually essential for evaluating experimental reaction rate data.

The half-life of a reaction, which is the time required for the concentration of a rate-determining reagent to decrease to half its initial value, is easily defined from integrated rate-law expressions. For example, for a first-order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

For reactions obeying second-order kinetics (i.e., when $\text{rate} = kc^2$),

$$t_{1/2} = \frac{1}{kc_0}$$

The latter half-life expression depends on the initial concentration of the reacting species and is not too satisfactory a method of expressing reactivity.

c. Related Environmental Scenarios. Many reactions of complexes involve changes in the composition of the coordination sphere. Reactions between metal ions and ligands fall in this category, since the "uncomplexed" metal ion is actually an aquo complex.

The facility of a particular complex ion to enter into reactions involving replacement of one or more ligands in its coordination sphere by others is termed its lability. Complexes for which reactions of this type are very rapid are called labile; those for which such reactions proceed slowly or not at all are termed inert. There is, of course, no sharp division of reactions into these categories; a continuous gradation of rates exists.

"Labile" and "inert" refer to rates of reaction. They must not be confused with the terms "stable" and "unstable," which refer to the thermodynamic tendency of species to exist under equilibrium conditions. Numerous examples are available to illustrate this important distinction. The stability of $\text{Ni}(\text{CN})_4^{2-}$, for example, is very high:



with $K \approx 10^{-22}$. However, the rate of exchange of CN^- ions with isotopically labeled CN^- added to the solution is immeasurably fast. In contrast, the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion will persist for days in an acid medium due to its kinetic inertness (or lack of lability), despite the fact that it is thermodynamically unstable:



with $K \approx 10^{25}$.

The rates of some chemical reactions are such that equilibrium is only slowly attained in the real system. In other chemical systems, equilibrium is established instantaneously. Taube has defined labile to mean systems in which reactions are complete (i.e., proceed to equilibrium) within the time of mixing. The term inert describes reactions that are either too slow to measure at all, or are slow enough to follow at ordinary conditions.

In aquatic environments, several classes of reaction are slow, proceeding with half-times of minutes or longer. These include certain metal-ion oxidations, oxidation of sulfides, sulfate reduction by organic substances, various metal ion polymerizations of metal-ion silicates and carbonates (e.g., dolomite), conversions among aluminosilicates (e.g., feldspar-kaolinite) and solution or precipitation of quartz.

d. Quantitative Applications in Environmental Problems. In the development of quantitative estimations of process kinetics, it is useful to classify reaction rates in a manner similar to Taube's description of labile and inert species. Thus, we can define the following categories:

- Rapid (R): $t_{1/2} < 1 \text{ sec}$
- Intermediate (I): $t_{1/2} = 1 \text{ sec to 1 year}$
- Slow (S): $t_{1/2} > 1 \text{ year}$
- N.A.: no information available
- N.C.: not of concern (e.g., the reaction does not take place)

These definitions are useful in systems of environmental interest, because reactions that are fast (compared with some arbitrary cut-off) will result in essentially complete equilibration and a speciation that can be based on equilibrium considerations. In slow reactions, a species will persist in its original form, and speciation calculations need not be attempted if, for example, only exposures within a short time frame are likely to be of concern. In the intermediate category, process reaction kinetics must be considered in more detail.

In organic reaction processes, a number of linear free-energy relationships (e.g., those based on increasing hydrocarbon chain length) can be used to estimate reaction rates or certain chemical properties. While such relationships have not been found for inorganic reactions, it is possible to correlate the general reaction rate characteristics of groups of compounds with factors such as electronic distribution, inner vs outer sphere reactions, complex geometry or the occurrence of substitution control in a reaction.

* Taube, H., Chem. Rev. 50:69 (1952).

The diversity of inorganic reaction rates and the lack of a unified theory that relates key parameters to those rates, emphasize the importance of empirical data. A principal goal of our approach, however, is to provide and summarize means of estimating whether particular reactions or classes of reactions proceed in time frames of environmental interest. Accordingly, we will classify reaction rates for various chemical groups according to the categories defined above. These classifications, which will be based on a review of rate constant data for various groups or classes of chemicals, will be summarized in a matrix similar to the following example:

Group	Reaction Type: Gas Phase		Liquid Phase, Homogeneous		
	Oxidation	Photolysis	Hydrolysis	Complex Formation	Polymerization
1)	R	NA	R	I	NC
2)	R	I	I	R	S
3)	S	S	NA	NC	I

Groups could be defined on the basis of periodic chart groupings, molecular class (e.g., organometallics with sigma bonds) or phase (solid, liquid, gas). For each matrix element in such a table, a discussion will be provided on the following important points:

- Availability and reliability of empirical data
- Availability of more detailed estimation methods or trends within the groups
- Environmental effects (temperature, catalysts, solvent, cosolutes)

We will attempt to organize and summarize relevant empirical data and experience in these matrices. For example, it is known that in the first transition series, virtually all octahedral complexes except those of Cr(III) and Co(III) are normally labile. Ordinary complexes equilibrate with additional ligands so rapidly that the reactions appear instantaneous by ordinary techniques of kinetic measurement. The complexes of Cr(III) and Co(III), in contrast, undergo ligand replacement reactions with half-times of the order of hours, days or even weeks at 25°C.

e. Estimation of Environmental Quantities Based on Process Kinetics. The factors or variables that influence the rates of reaction of complexes, aside from the usual factors such as temperature and catalyst materials, can include:

- the nature of the central metal ion,
- the nature of the leaving ligand,
- the nature of the entering ligand,

- the nature of the other ligands attached to the central atom,
- the charge on the complex,
- the nature of the solvent, and
- the presence of other ligands or metal ions in the solvent.

However, the only kinetic observation will be a rate law of the type described above.

Reactions involving water exchange and formation of complexes from aquo ions are useful in illustrating the effect of various factors on reaction rates. Nearly all such reactions are very fast, although a range of more than ten orders of magnitude is spanned by such "fast" processes.

Characteristic rate constants (sec^{-1}) for substitutions of inner-sphere H_2O of various aquo ions are summarized in Figure 2. Several interesting trends are apparent; for example, for the alkali and alkaline earth ions the influence of size and charge can be seen. Within each group, the rate of exchange increases with size, and for M^+ and M^{2+} ions of similar size, the ion with less charge exchanges more rapidly. While some series obey the radius rule--i.e., (Al^{3+} , Ga^{3+} , In^{3+}), (Sc^{3+} , Y^{3+}), and (Zn^{2+} , Cd^{2+} , Hg^{2+})--the divalent transition metals do not follow the charge and radius rules very well.

Extensive studies of the rates at which an aquo ion complex combines with a ligand to form a complex have revealed general rules that are valuable in estimation procedures:

- (1) The reaction rates for a given ion are practically independent (less than a factor of ten) of the identity of the ligand
- (2) The reaction rates for each ion are practically the same as the rate of water exchange for that ion, usually ≈ 10 times slower.

A widely stated explanation for these effects is that the formation reactions proceed in two steps: formation of the aquo ion-ligand or outer sphere complex, followed by elimination of H_2O from the aquo ion. It appears that there are few, if any, reactions in which a ligand is not first replaced by H_2O ; only then does the other ligand enter the complex by replacing H_2O . Hence the water exchange reaction rates and processes give useful information for estimating various process kinetics involving complexes. The Handbook will summarize data and trends similar to those presented in Figure 2. Taube has suggested that many of the available data pertaining to the reactivity of coordination compounds can be explained by trends in

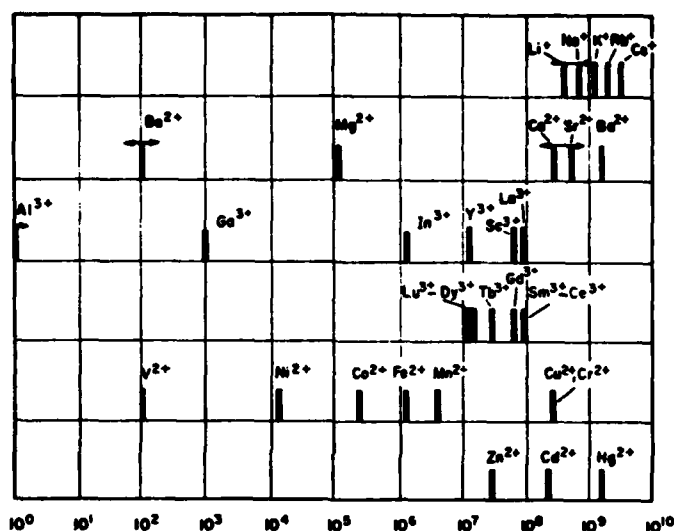


Figure 2. Characteristic rate constants (sec^{-1}) for substitution of inner sphere H_2O of various aquo ions.

Source: Cotton and Wilkinson, Advanced Inorganic Chemistry, 2nd edition, Wiley Interscience, 1966. (Reproduced with the permission of the publisher.)

electronic configuration as described by valence bond theory. In general, the labile complexes are either of the outer orbital type or of the inner orbital type with at least one vacant d orbital. On this basis, it is possible to construct tables summarizing labile and inert complexes for a large number of central metal ions, again illustrating the importance of the central ion in determining reaction rate. These data are particularly useful for inner orbital or d^2sp^3 complexes. We will summarize these relationships in groupings that provide the most complete and systematic presentation of available data. As part of our description of useful methods by which process kinetics of environment interest may be estimated, we will:

- describe the key differences in measurement techniques employed to study reaction kinetics; these techniques include static methods ($t_1 > 1 \text{ min}$), flow or rapid-mixing techniques ($1 \text{ min}^{-3} > t_1 > 10^{-3} \text{ sec}$), and relaxation methods ($t_1 < 10^{-3} \text{ sec}$);
- describe methods by which crystal field theory can be employed to consider and to predict the rates of substitution reactions;
- describe briefly the methods and equations by which experimental data are obtained and used to develop rate laws and rate constants;
- summarize current interpretations of kinetic processes based on electronic configuration of the central ion, donor and acceptor properties of the ligands, the nature of the linkage between the ligand and the central ion and the geometry of the complex; we will also consider the usefulness of evaluating the range of kinetic properties from mechanistic information;
- describe the relation between inner and outer sphere reaction rates and the methods by which Marcus-Hush concepts can be employed to estimate kinetic processes, especially for redox reactions; and
- evaluate which interpretive theories or approaches are most relevant to the environmental chemist. It is possible for a handbook user to avail himself of tables or matrices summarizing general relationships, if such exist, without being concerned with theory. This entails little risk of poor judgement.

4. Uptake by Biota

a. Purpose. Any discussion of pathways of inorganic constituents in the environment must include the potential for interaction with and effects on biota. This chapter will examine such interactions, with special emphasis on uptake of selected inorganic constituents by biota in a number of representative general ecosystem types. The purpose will be to focus on the present understanding of how certain inorganic constituents are taken up by different organisms, how they are managed by different biological systems, and the significance of biological fate processes. The latter subject will distinguish between the nature of uptake of organic (including organometallic) and inorganic constituents, including how biological levels can represent necessary micronutrient requirements, manageable levels, and levels that are potentially toxic to the organism, its offspring or to higher trophic levels of the food chain. The final purpose is to aid the reader in understanding how to find existing information and apply it to actual problems.

b. Content. The chapter will include discussions of uptake by biota in both terrestrial and aquatic (marine and freshwater) environments. Brief discussions of generalized pathways for contaminant fate, the nature of available information on such pathways, and the nature and likelihood of biological exposure, will introduce and provide a contextual framework for the chapter. This will be followed by a general discussion of our present understanding of how organisms respond to exposure to inorganic constituents under various environmental conditions. While the focus will be on uptake, transformation and loss processes related to exposure, the chapter will also examine the nature of toxicity and the significance of residual contaminant concentrations (residue measurements) in biota.

Voluminous information is available on the response of biota to inorganic constituents. Some of this specifically concerns uptake and its significance (e.g., to the food chain, the next generation, toxicity); however, except for the data in EPA "Criteria Documents," virtually all such information remains in individual research papers and texts and has not been tabulated or summarized. Accordingly, the "available data and criteria" section of the chapter will provide the following:

- (a) Selected, well-established criteria for "safe" levels of inorganic constituents in terrestrial and aquatic environments, such as land application standards and EPA water quality criteria.
- (b) Summary tables of known "normal" ranges of concentration and problematic concentrations of several of the most problematic inorganic constituents in each of the above environments. Known uptake levels, their consequences, and both mitigating and exacerbating circumstances will be noted. Preliminary examples of such tables are illustrated for terrestrial plants in Tables 7 and 8.

TABLE 7
Terrestrial Biota: Uptake by Plants, Normal Conditions
(Example Table Format)

<u>Inorganic Constituents</u>	<u>Known Normal Range and Conditions</u>	<u>Uptake/Consequences</u>
1. Cadmium (Cd)	Concentrations in some average soils. Comment on pH and other conditions as appropriate	Reported levels in crops, etc. Relationship of levels in biota to those in soil or water, if known.
2. Mercury (Hg)		
3		
4.		
5.		

TABLE 8
Terrestrial Biota: Uptake by Plants, Problematic Conditions
(Example Table Format)

<u>Inorganic Constituent</u>	<u>Problematic Ranges and Conditions</u>	<u>Uptake/Consequences</u>
1. Cadmium	a. Soil Concentrations b. and conditions such as c. pH.	Reported uptake levels, food chain, problems teratogenicity, toxicity, etc; effects of major variables, e.g. pH. Relationship of levels in biota to those in soil or water, if known.
2. Mercury		
3.		
4.		
5.		

This section of the chapter will explain how to apply this information to typical problems, noting the exceptions and difficulties associated with the data. It will also briefly discuss their implications and the insights that they provide with regard to data that are not available.

At present, we believe that the uptake of inorganic constituents by biota under field conditions is not a highly predictable event; the complexities of chemical and biological speciation combined with variable environmental conditions create formidable difficulties in generalizing about rates of inorganic uptake. This problem will be examined. Similarly, the nature, use, input, and output of some commonly used models will be described.

The chapter will also briefly discuss the types of chemical analyses used to improve the prediction or estimation of uptake by biota. Assumptions used for judging the availability of specific inorganic contaminants will be reviewed, as will levels of constituents in biota and how they are measured.

Finally, the chapter will conclude with summary generalizations concerning:

- How to use the information presented;
- Where to look for information concerning constituents not covered; and
- The outlook for improvement of the basis for estimation techniques.

5. Models for the Prediction of Environmental Fate

a. Objectives. The following material describes our approach to structuring Chapter 5 of the Inorganic Handbook, which will concern the use of models to predict the environmental fate of various inorganic pollutant chemicals. Our eventual choice for the structure and outline of the chapter reflects our objectives to:

- (1) reach as large a technical readership as possible, that is, to provide a useful guide to modeling for a broad spectrum of potential users who have technical backgrounds but little or no experience with the use of models;
- (2) create a sound technical document that modeling specialists would consider worth citing as a useful introduction to environmental modeling;
- (3) provide a description of currently important models which could stand on its own as a summary of the key features of those models; potential users would also be advised on the availability of the models, hardware requirements, and input requirements, etc; and
- (4) provide a "flowchart" approach that gives handbook users the essential information they need to select useful models, define limitations and issues of critical importance with respect to model usage, and define required steps in application of models to a particular problem. A related goal is to minimize the exposure of the user to large quantities of material that would not significantly enhance his ability to select or use available models.

Another important goal is to introduce the user to the applications, advantages and issues of model use in a way that is compatible with the conceptual methods and approaches employed in the models themselves. This overview of the modeling discipline should maximize the effectiveness of the user's time in considering models for his particular application and should guide his effort by pointing out problems and pitfalls at appropriate points.

b. Summary of Overall Approach. The chapter will be divided into four sections. The first, "General Considerations," will describe how to use the chapter, and will also provide general information needed by the user regardless of the specific model he employs or the specific environmental problem with which he is confronted. The essential general concepts, issues, approaches and requirements will be presented. Situations in which certain models are inappropriate will be noted.

The second section (5.2) will describe the kinds of environmental problems that might be considered for analysis with models. We believe that the most frequent user of this chapter will have some

technical background and limited modeling experience, and that he will consult the chapter with a specific environmental problem in mind. This section of the chapter will require the reader to think about his problem in the most general, generic way, since this approach is most useful for defining and selecting available models; thus, within each broad "Environmental/Pollutant Fate Scenario," a number of natural subdivisions are presented. These subdivisions provide a logical basis for model selection, because the concepts, limitations, approaches and issues associated with model use derive from the same situational considerations. The chapter gives the user a systematic and effective strategy to define, select and evaluate appropriate models and then directs him to appropriate models in Section 5.3.

Section 5.3 will describe the individual models that are important. While designed to stand on its own as a description of the models, it will provide specific information on the use of each model in the context of the problems defined in Section 5.2. The latter part of the section will describe and discuss aspects of modeling and calculation that are too specific to be included in Section 5.1.

The fourth section (5.4) will present sample problems for several models and environmental scenarios. The application of computer codes to solve problems is probably the clearest way to illustrate the use of individual models.

We believe that all potential model users must address a certain minimum set of issues and requirements before selecting and using any model. This information will be provided in Section 5.1 and should be read by all potential users. However, the outline is constructed so that the user can easily omit material that is unimportant or irrelevant to the problem at hand. Thus, depending on the particular environmental/ pollutant fate problem under consideration, the user may not have to read much of Sections 5.2 and 5.3.

c. Description of Proposed Sections.

(1) General Considerations (Section 5.1). The content of this section is clear from the detail provided in the outline. It will concentrate on the general issues that must be confronted by any prospective model user, regardless of the specific problem he is considering or the particular model he will ultimately use. It will also contain full instructions for using Chapter 5 and advice for problem definition prior to use of Section 5.2.

(2) Environmental/Pollutant Fate Scenarios (Section 5.2). Most environmental/pollutant fate scenarios have been classified according to their most general characteristics. The rationale is that these characteristics determine and define not only the conceptual issues important in analyzing the problem but also the ultimate selection of an appropriate model. In this section, the user can consult the particular "general" section pertinent to his problem, where he will find a discussion of some important aspects, advantages and issues

associated with the use of a model, followed by a reference to appropriate, specific models in Section 5.3. The user need not read all of Sections 5.2 and 5.3, because he will be directed to the most appropriate and pertinent material.

The broad categories in Section 5.2 are land, soil, groundwater, other underground, water, air and uptake by biota. Each of these subsections will describe the general features of the environmental/pollutant fate and exposure scenario and the rationale for further subdividing that general category.

For example, the "land" category, which will have a subcategory for each of the conceptual processes to be modeled, will include a disposal scenario that considers a pile of some form of waste or pollutant. One important process to be considered is leaching, i.e. the solubilization of chemical constituents from the waste or polluting material. The other constituent processes to be modeled here are quite different from those associated with land treatment or disposal related to agricultural practices (e.g., spraying of pesticides). Pollutant movement is generally lateral in land scenarios and vertical in soil modeling; in groundwater modeling, pollutant movement can be both vertical and horizontal.

The "soil" section (5.2.3) will also have several subdivisions. In the land disposal scenario, soil pollution is a function of the leaching rate in a pollutant mass (pile) and the hydrogeologic conditions underneath the pile. In the land treatment scenario, pollutants are dispersed and homogeneously mixed within the soil layer. Pollutant leaching depends upon net rainfall infiltration in the soil. For storage-related processes, the rate of pollutant migration is a function of the moisture velocity in the soil zone. Finally, for injection processes, pollutants move both vertically and laterally from a point source, forming a cone; their rate of migration is a function of injection pressure.

Groundwater scenarios (5.2.4) will require fewer subdivisions: for areal processes, pollutant fate and modeling dependent upon the waste site and hydrologic characteristics; for the point source in aquifer scenarios, pollutant fate is a function of injection rate, nature of materials and aquifer characteristics. The scenarios will also cover various groundwater flow alteration processes including interception and dilution.

"Other Underground" (5.2.5) is not intended to be a detailed section. It will briefly summarize the approaches being taken in modeling processes related to nuclear waste disposal in granite, salt, tuff, basalt, etc. The large body of research in this area will be referred to and summarized, but no attempt will be made to provide a full description of the modeling processes because of their narrow applicability.

Models of water processes (Section 5.2.6) fall into four main categories -- land/pond/reservoir, stream, estuary and ocean. Several subcategories must be considered, to take into account some important technical and conceptual differences associated with modeling these types of processes. For example, it is important to know whether a pollutant originates at a point source or not. The presence of sediment is handled somewhat differently in each category. Other important issues are whether the water environment is moving or still and saline or non-saline.

In the lake/pond/reservoir scenario of Section 5.2.6, several kinetic issues affect the modeling of pollutant fate. Since a lake is usually non-moving, thermocline effects are important with respect to pollutant mixing; while point discharge is important, non-point sources must also be considered. A pond is also usually non-moving, but thermocline and surface runoff are of minor importance. A reservoir is similar to a pond, except for the possible accumulation of contaminated stream sediment.

A stream has the characteristics of flow and sediment. In point-source stream contamination, both the near-field and far-field zones must be considered. In non-point source contamination, only far-field issues are important.

In estuary modeling, flow velocities are much lower than in a stream. Important technical differences also derive from the presence of much finer sediment in the clay zone and from the presence of some salinity.

In ocean scenarios, there is very little water flow to consider, but circulation does cause mixing. A sand sediment is encountered rather than clay, so a totally different distribution of sediment must be modeled. Salinity is, of course, an important factor.

(3) Models (Section 5.3). As described earlier, the chapter will be organized so that the crucial issues associated with use of a model will be difficult to ignore. The user will not be likely to attempt to use a model in inappropriate applications and with wholly unrealistic expectations. However, we also intend that the description of the models be useful to another kind of reader -- one who wants to learn more about individual models and their uses. Accordingly, we have attempted to design Section 5.3 so that it can stand on its own.

The introduction, Section 5.3.1, will describe both the general groupings of models and the iterative manner in which improvements are made to existing models. The user should be aware that certain models (e.g., EQ3) are descendants of earlier models (e.g., WATEQ) and that the newer versions usually incorporate all the features of the earlier models. We will provide a chart or figure that summarizes the lineage of important models.

Subsection 5.3.2 will describe the actual models. It will begin with a summary table and flowchart similar in principle to that shown below to summarize the models covered and their uses and applications in various environmental categories.

APPLICABILITY OF MODELS

<u>Model</u>	<u>Land</u>	<u>Soil</u>	<u>Groundwater</u>	<u>Water</u>
GEOCHEM	--	*		*
WATEQ	--	--	*	*
SESOL	*	*	*	--

In choosing a structure for this section, we considered the fact that some models can be used for more than one environmental application. Partly for this reason, and partly to present a complete and logical coverage of available models, we concluded that a separate subsection should be devoted to each model. Alternative approaches, such as grouping various models and issues by application, would result in unnecessary repetition. Three topics will be discussed for each model:

- Description
- Uses
- Data requirements
- Form and content of output
- Availability (source, cost)
- Hardware requirements
- Key references

In the description section, we expect to cover the following:

- Processes (which are modeled)
- Concepts employed
- Designated uses and applications
- Mathematical techniques
- Computer codes (where? verified? etc.)

In the "uses" subsection, we will outline specific characteristics, issues and requirements associated with use of the model in a particular environmental situation (e.g., use of SESOL as a soil model). In this way, we can describe how the model is used in several different applications.

Subsection 5.3.3, Modeling/Calculation Issues, will provide important information related to the use of models that is too specific to be included in Section 5.1. We will discuss practical ramifications of model use for the subject areas listed in our summary, and will describe the methods by which existing models simulate the underlying processes. (The topics we will consider were summarized in Table 6.)

Speciation and the calculation of activity coefficients in electrolyte environments will be given special attention, since this important problem affects the applicability of most models and the usefulness of most estimation methods.

In addition to the above, this section will contain a summary listing of commonly-used dispersion models that might be appropriate for each environmental medium/scenario. References will be provided to other manuals where detailed information may be found.

PART II - THE ENVIRONMENTAL PROPERTIES OF IMPORTANT ELEMENTS,
LIGANDS AND CHEMICAL CLASSES

Overview

Part I of the Handbook will have described specific methods for estimating the properties of chemicals that have a significant influence on their stability, fate and transport in environmental media. Methods will be provided for estimating both equilibrium and kinetic properties, and for selecting and using environmental transport and fate models that require such properties as input.

To further assist the reader, Part II (Chapters 6-10) will summarize information on applying the estimation methods and models of Part I to assess the behavior of specific inorganic compounds and families of compounds in the air, water and soil environments.

We will first provide information on the properties and processes of major or matrix components of water and soil systems that are important to an understanding of the fate and transport of trace or pollutant species. We will next provide information on the interactions of trace or pollutant metal species with major and important trace ligands in each environmental compartment. We will then provide information on trace or pollutant ligands and their behavior in each baseline or matrix compartment. A final section will provide both general and chemical-specific information on several chemical classes of interest.

6. Major/Matrix Elements and Ligands

The elements that will be treated in this section of the Handbook are:

- Sodium
- Potassium
- Calcium
- Magnesium
- Silicon
- Aluminum
- Iron

The first four are the alkali (Na and K) and alkaline earth (Ca and Mg) elements, which constitute the major metallic portion of dissolved solids in natural waters. The last three (Si, Al and Fe), in combination with oxygen, constitute the major portion of the mineral fraction of natural soils.

The following major ligands are typically associated with each of the above elements in natural systems and will also be treated in this section of the Handbook:

- Hydroxyl (OH^-)
- Chloride (Cl^-)
- Sulfate (SO_4^{2-})
- Carbonate (CO_3^{2-}) and Bicarbonate (HCO_3^-)

a. Properties and Speciation in Water. About 99% of the dissolved solids content of natural waters is made up of five cationic components (H^+ , Na^+ , Ca^{+2} , Mg^{+2} and K^+) and four anionic ligands (OH^- , Cl^- , SO_4^{+2} and CO_3^{+2}). This means that an aquatic system is essentially defined once the concentration of each of these components has been specified at a given temperature or pressure. These major components interact within the aquatic system to form a very large number of ionic and covalent species. An example of the former is the interaction of H^+ and CO_3^{+2} to form HCO_3^- . An example of the latter is the interaction of H^+ and OH^- to form H_2O .

The Handbook will include the results of equilibrium calculations for major component interactions in fresh waters and sea water. The primary results are the nature and concentration of species present at equilibrium. These results can be particularly useful in estimating the activities of trace or pollutant ions in natural waters, for two reasons:

(1) The activity of a pollutant ion depends upon the ionic strength of the solution. This, in turn, will be approximately equal to the ionic strength of the major or matrix components, if pollutant concentrations are small relative to matrix component concentrations.

(2) The introduction of a trace metal or ligand to a natural water system generally does not change the activities of major or matrix components. This greatly simplifies calculations of pollutant speciation or complexation with major components.

b. Properties and Speciation in Soil. The alkali and alkaline earth metals, which are the major cationic components of natural waters, account for less than 4% of the elemental composition of the average soil; but it is these elements and the hydroxyl group ($-OH$) that are key determinants in the mineralogy of the soil and therefore its chemistry. Over 90% of the elemental composition of the average soil consists of oxygen, silicon, aluminum and iron, which contribute very little to the dissolved solids concentration of natural waters.

Soil is a highly complex material, whose properties cannot be adequately described by its elemental composition. Soil consists of many solid or mineral phases, a liquid or aqueous solution phase, and a gas phase ("soil air"), all in dynamic equilibrium. The Handbook will provide:

- Thermodynamic data relevant to the stability of the major silicon-, aluminum- and iron-containing minerals in natural soils;

- Graphs, or other appropriate representation, of the composition of soil water in equilibrium with the major soil minerals, generally as a function of pH;
- Thermodynamic data on equilibrium among CO_2 in soil air, carbonate and bicarbonate species in soil solution, and carbonate minerals in soil solids, as a function of pH;
- Cation exchange capacities of common soil minerals, which are important to: predicting adsorption of trace or pollutant cations, their distribution (among soils, groundwater, sediments and surface water) and their transport in ground and surface waters.

7. Trace or Pollutant Metals and Metalloids

a. Coverage. The Handbook will cover the following trace or pollutant metals (or metalloids):

- | | |
|-------------|-------------|
| • Antimony | • Manganese |
| • Arsenic | • Mercury |
| • Barium | • Nickel |
| • Beryllium | • Selenium |
| • Cadmium | • Silver |
| • Chromium | • Thallium |
| • Copper | • Zinc |
| • Lead | |

As indicated in Table 9, this list includes the thirteen metals designated as priority pollutants under the Clean Water Act, the eight metals for which there are interim primary drinking water standards and which are analyzed in determining whether a hazardous waste is EP-toxic, the two metals currently regulated as hazardous air pollutants, and the four metals currently on the Cancer Advisory Group's list. There is considerable overlap among the various lists.

For each metal, the predominant inorganic species in the environment will be covered. These will generally involve the following ligands, although (as indicated in Table 10) each ligand will not necessarily be included for each metal:

- Hydroxide
- Chloride
- Sulfate
- Carbonate/bicarbonate
- Sulfide
- Oxide
- Silicate
- Hydrosulfide

 * A waste is "EP-Toxic" if a specified extraction procedure test yields an extract containing concentrations of certain toxic chemicals above specified levels.

TABLE 9
THE OCCURRENCE OF METALS IN VARIOUS "REGULATORY" LISTS

Priority Pollutant	TSCA Section 5	TSCA Section 4	40CFR 141, 143 Drinking Water Std.	40CFR 61 Hazardous Air Pollutant	CAG List	40CFR 261 RCRA	29CFR 1910 OSHA
Aluminum	-	-	-	-	-	X	-
Antimony	X	-	-	-	-	H XX	X C
Arsenic	X	XX	X	-	X	EH XX	C
Barium	-	-	X	-	-	EH X	C
Beryllium	X	-	-	X	X	X	X C
Boron	-	-	-	-	-	-	C
Cadmium	X	-	X	-	X	E XX	X
Calcium	-	X	-	-	-	HT X	C
Chromium	X	-	X	-	-	E XX	C
Cobalt	-	X	-	-	-	-	X
Copper	X	-	X (sec)	-	-	H X	X
Gold	-	-	-	-	-	-	-
Iron	-	-	X (sec)	-	-	T X	X C
Lead	X	X	X	-	-	EHT XX	C
Lithium	-	-	-	-	-	-	C
Magnesium	-	-	-	-	-	-	C
Manganese	-	-	X (sec)	-	-	-	C
Mercury	X	-	X	X	-	EHT XX	X C
Nickel	X	-	-	-	X	H XX	X C
Osmium	-	-	-	-	-	H X	C
Platinum	-	-	-	-	-	-	C
Potassium	-	XX	-	-	-	H X	-
Rhodium	-	X	-	-	-	-	X
Selenium	X	-	X	-	-	ET X	C
Silicon	-	XX	-	-	-	-	C
Silver	X	-	X	-	-	E X	X C
Sodium	-	XX	-	-	-	H X	C
Strontium	-	-	-	-	-	H X	-
Thallium	X	-	-	-	-	HT X	-
Tin	-	X	-	-	-	-	C
Titanium	-	X	-	-	-	-	C
Vanadium	-	-	-	-	-	H X	X C
Zinc	X	X	X (sec)	-	-	H X	C

E = EP Toxicity; H = Hazardous; T = Toxic; C = Compounds; XX = frequent occurrence; sec = secondary

TABLE 10

PREDOMINANT INORGANIC SPECIES FOR SEVERAL TRACE METALS
IN AQUATIC SYSTEMS

<u>Metal</u>	<u>Predominant Ligands</u>	<u>Predominant Species</u>
Ba	Sulfate	$\text{BaSO}_4(\text{s})$
	Carbonate	$\text{BaCO}_3(\text{s})$
Cd	Chloride	CdCl^+ , CdCl_2 , CdCl_3^-
	Hydroxide	CdOH^+
	Sulfide	CdS
	Hydrosulfide	CdHS^+ , $\text{Cd}(\text{HS})_2$, $\text{Cd}(\text{HS})_3^-$, $\text{Cd}(\text{HS})_4^{-2}$
	Carbonate	$\text{CdCO}_3(\text{s})$
	Hydroxide	$\text{Cd}(\text{OH})_2(\text{s})$
Cr	Hydroxide	$\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$, $\text{Cr}(\text{OH})_3(\text{s})$
	Oxide	CrO_4^{-2}
	Other	HCrO_4
Cu	Carbonate	CuCO_3 ,
	Hydroxide	CuOH^+ , $\text{Cu}(\text{OH})_2(\text{s})$
	Sulfides	$\text{CuS}(\text{s})$
	Oxides	$\text{CuO}(\text{s})$
	Other	$\text{CuFeS}_2(\text{s})$,
		$\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s})$ $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$

TABLE 10
 PREDOMINANT INORGANIC SPECIES FOR SEVERAL TRACE METALS
 IN AQUATIC SYSTEMS (CONTINUED)

<u>Metal</u>	<u>Predominant Ligands</u>	<u>Predominant Species</u>
Pb	Chloride	PbCl^+ , PbCl_2 , PbCl_3^-
	Hydroxide	PbOH^+ , $\text{Pb(OH)}_2(\text{s})$
	Carbonate	PbCO_3 , $\text{PbCO}_3(\text{s})$
	Sulfide	$\text{PbS}(\text{s})$
	Oxide	$\text{PbO}_2(\text{s})$
Hg	Chloride	HgCl^+ , HgCl_2 , HgCl_3^-
	Hydroxychloride	HgOHCl
	Hydroxide	Hg(OH)_2 , $\text{Hg(OH)}_2(\text{s})$
	Sulfide	HgS_2^{-2} , $\text{HgS}(\text{s})$
	Hydroxysulfide	HgOHS^-
Ni	Chloride	NiCl_2
	Sulfate	NiSO_4
	Sulfide	$\text{NiS}(\text{s})$
	Hydroxide	$\text{Ni(OH)}_2(\text{s})$
Ag	Chloride	AgCl , AgCl_2^- , $\text{AgCl}(\text{s})$
	Sulfide	AgS^- , $\text{Ag}_2\text{S}(\text{s})$
	Hydrosulfide	AgHS , AgHS_2^{-2} , Ag(HS)_2^-
	Bromide	$\text{AgBr}(\text{s})$
Zn	Chloride	ZnCl^+
	Sulfate	ZnSO_4
	Hydroxide	ZnOH^+
	Carbonate	ZnCO_3 , $\text{ZnCO}_3(\text{s})$
	Sulfide	ZnS , $\text{ZnS}(\text{s})$
	Silicate	$\text{ZnSiO}_3(\text{s})$

Source: F.M.M. Morel, Principles of Aquatic Chemistry, John Wiley and Sons, New York, 1983. (Reproduced with permission of the publisher.)

b. Information to be Provided for Each Metal (or metalloid). The Handbook will include a short section on each of the 14 elements listed above, organized as follows:

(1) Properties of the Elements

- Table giving:
 - atomic weight
 - atomic number
 - stable valence states
 - principal compounds produced, annual production rates and principal uses of each compound

(2) Fate Processes in Aquatic Environments

- Fresh Waters
 - Major dissolved species at equilibrium as a function of pH and pE [Pourbaix diagram(s) or other appropriate representation(s)]
 - Precipitation
 - Adsorption to sediments
 - Volatilization
- Sea Waters
 - Major dissolved species at equilibrium as a function of pH and pE [(Pourbaix diagram(s) or other appropriate representation(s)]
 - Precipitation
 - Adsorption to sediments
 - Volatilization

(3) Fate Processes in Soils

- Thermodynamic properties of principal ores (minerals)
 - e.g., free energies of dissociation, oxidation/reduction and acid/base reactions
- Adsorption as a function of pH and pE
- Precipitation/dissolution equilibria; equilibrium composition of soil water
- Volatilization*

8. Trace or Pollutant Ligands

a. Coverage. The preceding chapter will have covered metals and associated ligands (both major and trace) for which the metal is the element of primary environmental concern. Chapter 8 will cover trace or pollutant ligands of primary environmental importance or concern,

* Only important for As, Se and Hg.

independent of the metal with which they may be associated. Groups of ligands, defined by their principal element of environmental interest, will be treated together as follows:

- Nitrogen-containing ligands (cyanide, ammonia, nitrate, nitrite, organic amines (e.g., EDTA, NTA))
- Sulfur-containing ligands (sulfide, hydrosulfide, thiosulfate, sulfite, sulfate, polysulfide, polythionite and polythionates)
- Phosphorus-containing ligands (phosphate, phosphite, polyphosphates)
- Fluoride
- Bromide

The first three groups contain elements essential to the formation of living matter. The concentrations and forms of these elements in the environment are partially controlled by soil microorganisms.

b. Information to be Provided. The treatment of each group of ligands in the Handbook will be slightly different, depending upon the environmental factors that control the cycle of each element and the role played by each element in controlling the master environmental variables, pH and pE.

(1) Nitrogen-Containing Ligands

- The Nitrogen Cycle (very brief summary)
- Stability of Nitrogen Species in Water and Soils
 - Equilibrium constants for nitrogen reactions in the environment
 - Pourbaix diagrams displaying concentration of nitrogen species as functions of pE and pH
- Kinetics of Nitrogen-containing Species
- Cyanide Complexes
 - Structure
 - Stability constants
 - Fate Processes in waters and soils
- Ammonia Complexes
 - Structure
 - Stability constants
 - Fate processes in waters and soils

(2) Sulfur-containing Ligands

- The Sulfur Cycle (very brief summary)
- Stability of Sulfur Species in Soil and Water
 - Important sulfur-containing species
 - Equilibrium relationships among sulfur-containing species as a function of pE (dominant factor)
- Role of Sulfides in Controlling Metal Activities
 - Stability of sulfide minerals and solids as a function of pH and pE

- Stability of soluble sulfide complexes as a function of pH and pE.

(3) Phosphorus-containing Ligands

- The Phosphorus Cycle (very brief summary)
- Equilibrium Constants for Reactions of Phosphates
 - Acid dissociation
 - Precipitation/dissolution
 - Oxidation/reduction
 - Hydrolysis
- Fate Processes in Water and Soils

(4) Fluoride

- Stability of Principal Fluoride Minerals
- Fate Processes in Waters
- Fate Processes in Soils

(5) Bromide

- Principal Bromine-containing Compounds
- Fate Processes in Waters
- Fate Processes in Soils

9. Radionuclides

In our extended discussion of specific radioelements, we will focus on those nuclides that are likely to exist in the environment as the result of natural causes or human activities. This selection will permit a relatively small group of substances to be described in appropriate detail, with emphasis on characteristics that may be particularly important for effective environmental management.

A useful division can be made into two general groups:

- (a) Radionuclides that have natural origins, such as uranium and thorium and their radioactive daughter products, which are of primordial terrestrial origin, together with those like tritium and ¹⁴-carbon that are cosmogenic in origin and are therefore continuously resupplied; and
- (b) Radionuclides that are either partly or entirely produced by artificial means. For example, ¹⁴-carbon is produced artificially for use as a radio-tracer and ultimately becomes mingled in the environment with the naturally generated material, although the condition of its chemical attachment can influence its distribution and fate in the near term. ⁹⁹-Technetium, on the other hand, is produced entirely by artificial means.

Tables 11 and 12 provide preliminary lists of radionuclides in each of these two groups; modifications of the actual coverage will be made during the course of the Phase II work.

The amount of these radionuclides that may be present in the environment and constitute a problem to environmental management will vary in unpredictable ways in some instances, and will be relatively constant and predictable in others. These cases will be identified and described in the Handbook.

The issue of successive decay and the formation of radioactive (and therefore hazardous) daughter nuclides is of particular interest, since entirely new elemental species are formed thereby. The concentrations of the new species are usually extremely small, presenting special problems for management and treatment. For instance, the successive decay products of ²³⁸-uranium include several that have no stable isotopes with which to commingle in nature. Their behavior in the environment is initially that of single atoms, widely dispersed in an alien environment.

The understanding and control of such materials calls for an appreciation of the physical laws governing the behavior of extremely small quantities of matter. Some of this information is available in the literature, but the subject presents unusual difficulties for experimental verification of theory. Valid experimental data may

TABLE 11

SOME RADIONUCLIDES FROM THE NATURAL DECAY OF 238-Uranium

<u>Isotope</u>	<u>Symbol</u>	<u>Principal Radiation</u>	<u>Half-Life</u>	<u>Atoms per pCi</u>
226-radium	^{226}Ra	α (4.78 MeV)	1620 y	2.7×10^9
222-radon	^{222}Rn	α (5.49 MeV)	3.8 d	1.77×10^4
218-polonium	^{218}Po	α (6.00 MeV)	3.05 m	9.8
214-lead	^{214}Pb	β, γ	26.8 m	85.8
214-bismuth	^{214}Bi	β, γ	19.7 m	63.1
214-polonium	^{214}Po	α (7.68 MeV)	1.6×10^{-4} s	8×10^{-6}
210-lead	^{210}Pb	β	22 y	3.7×10^7
210-polonium	^{210}Po	α (5.30 MeV)	138 d	6.4×10^5

Table 12
SELECTED RADIONUCLIDES WITH HALF-
LIVES GREATER THAN 1 YEAR

Radionuclide	Common name	Half-life (years)	Specific activity (Ci/g)
³ H	Tritium	1.2 × 10 ¹	9.7 × 10 ⁴
¹⁴ C	Carbon-14	5.7 × 10 ⁴	4.5
²² Na	Sodium-22	2.6	6.3 × 10 ³
⁵⁵ Fe	Iron-55	2.7	2.4 × 10 ³
⁵⁹ Ni	Nickel-59	8.0 × 10 ⁴	7.6 × 10 ⁻³
⁶³ Ni	Nickel-63	1.0 × 10 ⁵	5.7 × 10 ³
⁶⁰ Co	Cobalt-60	5.3	1.1 × 10 ³
⁸⁵ Kr	Krypton-85	1.1 × 10 ⁵	3.9 × 10 ³
⁹⁰ Sr	Strontium-90	2.9 × 10 ⁴	1.4 × 10 ³
⁹⁹ Tc	Technetium-99	2.1 × 10 ⁵	1.7 × 10 ⁻²
¹²⁹ I	Iodine-129	1.6 × 10 ⁷	1.7 × 10 ⁻⁴
¹³⁴ Cs	Cesium-134	2.1	1.3 × 10 ³
¹³⁵ Cs	Cesium-135	2.3 × 10 ⁶	1.2 × 10 ⁻³
¹³⁷ Cs	Cesium-137	3.0 × 10 ⁴	8.7 × 10 ³
¹⁴⁷ Pm	Promethium-147	2.6	9.4 × 10 ³
¹⁵⁴ Eu	Europium-154	8.6	2.7 × 10 ³
²²⁶ Ra	Radium-226	1.6 × 10 ³	9.9 × 10 ⁻¹
²³⁵ U	Uranium-235	7.1 × 10 ⁸	2.1 × 10 ⁻⁴
²³⁸ U	Uranium-238	4.5 × 10 ⁹	3.3 × 10 ⁻⁷
²³⁹ Pu	Plutonium-239	8.8 × 10 ⁴	1.7 × 10 ³
²⁴¹ Pu	Plutonium-241	14.3	6.2 × 10 ⁻³
²⁴¹ Am	Americium-241	4.3 × 10 ²	3.4

Source: CRC Handbook of Environmental Radiation,
A.W. Klement, Jr. (ed.), CRC Press, Inc.
Boca Raton, FL, 1982. (This table adapted
by Klement from copyrighted information
published in Chart of the Nuclides, 11th ed.,
published by General Electric Co., San Jose,
CA. Permission to reproduce this information
was granted by General Electric Co.)

be difficult to obtain and organize, except on an element-by-element and case-by-case basis. To achieve this end, we will search the current literature and obtain supplementary data wherever possible from scientists who are currently active in the field.

Another important aspect of radionuclide behavior in the environment is that of the effect of chemical and physical forces on the comingling of isotopes. Two examples of this are ^{14}C -carbon and the three most commonly used radioisotopes of iodine (^{125}I , ^{129}I and ^{131}I). Radiocarbon may be produced either in an organic or inorganic combination (e.g., methane or carbon dioxide), and iodine may be produced as an alkali-salt or an organic form such as methyl iodide. The rate of dilution of the radioisotope in the presence of stable isotopes of the element largely depends on the thermodynamic stability (i.e., chemical bond stability) of the initial chemical combinations of each isotope. These isotopic dilution phenomena are thus closely related to thermodynamic equilibria; however, if the radioisotope is initially produced "carrier-free," the combined forms may be present in such small amounts that the principles of chemical equilibria are not strictly obeyed.

10. Chemical Classes

a. Overview. We propose that the Phase II Handbook provide relevant environmental property data on the following 18 chemical classes:

- | | |
|----------------------------|-------------------------------|
| • Organometallics | |
| • Acids | |
| • Anionics | <u>Major classes based on</u> |
| • Salts | properties and/or |
| • Oxides | constituents |
| • Gases | |
| • S-Containing | |
| • P-Containing | <u>Major classes based on</u> |
| • Si-Containing | compounds of a specific |
| • B-Containing | element |
| • Bases (hydroxides) | |
| • Carbonyls | |
| • Carbides | |
| • Cyanides | <u>Minor classes based</u> |
| • Hydrides | primarily on |
| • Hypochlorites, chlorates | constituents |
| • Peroxides | |
| • Binary compounds | |

This list of classes resulted from a review of several compilations of chemical lists representing, for example, major inorganic chemicals produced, inorganic chemicals reviewed by the EPA under the Toxic Substance Control Act, chemicals regulated in the workplace by OSHA, and hazardous chemicals regulated by RCRA. It thus represents chemical classes of commercial importance and those considered to be problematic (from an environmental or worker health viewpoint) by federal regulatory agencies. It is subject to possible future revision to reflect comments on this Phase I report and our initial work in Phase II.

Examples of chemicals in each of the chosen classes are provided in Table 13. These chemicals were extracted from one or more of the lists mentioned above. Our intent in Phase II is to revise (and extend, if necessary) the list of specific chemicals in each class and then to provide relevant environmental data for the identified compounds.

There is clearly some overlap between the chemical classes listed above and the elements and ligands proposed to be covered in Chapters 6, 7, and 8 of the Handbook. Silicon, for example, is currently listed in two places (the element in Chapter 6 and its compounds here). Also, cyanide would be covered as a pollutant ligand in Section 8.1 and as a class of interest here. We will ensure that these sections of the Handbook are coordinated to avoid direct overlap.

* Organometallics are covered in subsection b below.

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METHODS FOR ESTIMATING PHYSICOCHEMICAL PROPERTIES OF
INORGANIC CHEMICALS O. (U) LITTLE (ARTHUR D) INC
CAMBRIDGE MA W J LYMAN ET AL. JUN 84 ADL-C-50075

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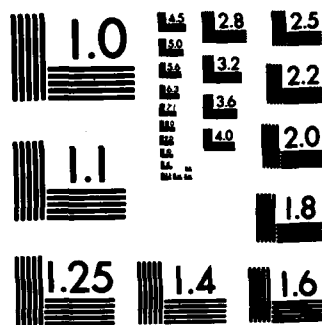
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 13. EXAMPLES OF CHEMICALS IN CHEMICAL CLASSES CHOSEN

(Excluding organometallics which are listed in
Tables 14-18)

1. ACIDS

Nitric
Phosphoric
Sulfuric
Hydrochloric
Hydrofluoric
Chlorosulfonic
Chromic
Arsenic
Selenious
Hydrogen Sulfide

2. ANIONICS

Ammonium Molybdate
Sodium Molybdate
Sodium Chromate
Sodium Dichromate
Potassium Permanganate
Fluorides
Lead Arsenate
Lead Chromate
Zinc Chromate
Ammonium
Calcium
Chromates
Thallium (I) Selenite

3. SALTS

Ammonium Nitrate
Calcium Carbonate
Sodium Chloride
Aluminum Sulfate
Ammonium Sulfate
Sodium Carbonte (Soda Ash)
Potassium Chloride
Ferrous Sulfate
Potassium Sulfate
Sodium Sulfate
Aluminum Chloride
Aluminum Fluoride
Ferric Chloride
Ammonium Chloride
Barium Carbonate
Copper Sulfate
Magnesium Sulfate

Manganese Sulfate
Potassium Carbonate
Potassium Acetate
Sodium Propionate
Strontium Carbonate
Zinc Sulfate
Calcium Sulfate (Gypsum)
Iron Salts
Carbonic Acid, Dithallium Salt
Lead Acetate
Lead Subacetate
Sulfuric Acid, Thallium
Salt
Thallium Carbonate
Thallium Chloride
Thallium Nitrate
Thallium Sulfate

TABLE 13. (CONTINUED)

4. OXIDES

Aluminum Oxides
Titanium Dioxide
Molybdic Oxides
Zinc Oxide
Antimony Oxide
Cuprous Oxide
Vanadium Oxide
Zirconium Oxide
Antimony Trioxide
Cadmium Oxide
Calcium Oxide
Chlorine Dioxide
Chromium Oxides
Iron Oxides
Magnesium Oxide
Manganese Tetroxide
Nitric Oxide
Nitrogen Dioxide
Osmium Tetroxide
Arsenic (III) Oxide
Arsenic (V) Oxide
Selenium Dioxide
Thallium (III) Oxide
Vanadium Pentoxide

5. GASES

Ammonia
Carbon Dioxide
Sulfur Dioxide
Carbon Monoxide
Cyanogen
Cyanogen Chloride
Hydrogen Bromide
Hydrogen Chloride
Hydrogen Fluoride
Nitrogen Trifluoride
Oxygen Difluoride
Selenium Hexafluoride
Hydrogen Sulfide
Ozone

6. S-CONTAINING

Carbon Disulfide
Sodium Sulfite
Sodium Hydrosulfide
Sodium Hydrosulfite
Sodium Thiosulfate
Hydrogen Sulfide
Nickel Sulfide
Sodium Bisulfite
Sodium Metabisulfite
Sulfur Dioxide
Sulfur Hexafluoride
Sulfur Monochloride
Sulfur Tetrafluoride
Sulfuryl Fluoride
Selenium Disulfide
Strontium Sulfide
Sulfur Hydroxide
Polysulfides of Na and K

7. P-CONTAINING

Calcium Phosphate
Diammonium Phosphate
Calcium Phosphate, Dibasic
Sodium Phosphate, Tripoly
Phosphorus Pentasulfide
Phosphorus Trichloride
Sodium Hexametaphosphate
Sodium Metaphosphate
Tribasic Sodium Phosphate
Phosphorus Oxychloride
Phosphorus Pentoxide
Potassium Pyrophosphate
Tetrapotassium Pyrophosphate
Sodium Hypophosphite
Monobasic Sodium Phosphate
Dibasic Sodium Phosphate
Tetrabasic Sodium Phosphate
Tetrasodium Pyrophosphate
Phosphine
Phosphorus Pentachloride
Aluminum Phosphide
Lead Phosphate
Zinc Phosphide

TABLE 13 (CONTINUED)

8. Si-CONTAINING

Talc
Sodium Silicates
Sodium Meta and Orthosilicate
Calcium Silicate
Silicone
Silicon Tetrahydride
Silica
Silicates
Asbestos minerals:
 Chrysotile
 Crocidolite
 Amosite

10. BASES/HYDROXIDES

Caustic Soda
Lime
Caustic Potash
Cesium Hydroxide

12. CARBIDE

Calcium Carbide
Silicon Carbide

14. HYDRIDES

Arsine
Germanium Tetrahydride
Hydrogen Selenide
Lithium Hydride

16. PEROXIDES

Hydrogen Peroxide

9. B-CONTAINING

Borax
Borates
Boric Acid
Boron Oxide
Boron Tribromide
Boron Trifluoride
Pentaborane

11. CARBONYL

Phosgene
Carbonyl Fluoride
Nickel Carbonyl

13. CYANIDES

Hydrogen Cyanide
Barium Cyanide
Calcium Cyanide
Copper Cyanide
Nickel Cyanide
Zinc Cyanide
Selenium Cyanide
Potassium Cyanide
Potassium Silver Cyanide
Silver Cyanide

15. HYPOCHLORITE, CHLORATE

Sodium Chlorate
Calcium Hypochlorite

17. BINARY COMPOUNDS

Bismuth Telluride
Bromine Pentafluoride
Chlorine Trifluoride

The information supplied for a given chemical class will depend largely on its environmentally important properties. For each class we would first present a general discussion of the class, the types of compounds that represent it, and the key properties that control its fate and transport in the environment. Data would then be provided for specific chemicals in that class. We expect that the chemicals chosen will, to the extent possible (i.e., based on availability of data) be those listed in Table 13; others will be added if meaningful (and representative) data are available for them.

Under "Acids," for example, the general discussion will describe the concept of, and properties defining, strength; this will be cross-referenced to Section 2.3.3 ("Acid-Base Equilibria and Hydrolysis"). The formula for calculating the percent dissociation as a function of pH would be given. The discussion will also cover the distinction between mono-, di- and tri-protic acids, the properties of oxidizing acids, and other features. Data will be included on, for example, acid dissociation constants, oxidation potential, and information relating to the fate of the ions generated.

For oxides, the general discussion will be followed by data (or information) on solubility product constants, acid/base behavior, and role in redox reactions.

For gases, the initial discussion will be followed by tabulated data on vapor pressures (including boiling points), water solubilities, Henry's law constants, adsorption on solids, and other pertinent properties.

Organometallics will be given particularly extensive coverage in the Phase II Handbook, as described below.

b. Organometallic Compounds (Section 10.1)

(1) Overview. There are several reasons for covering organometallic compounds in the Handbook:

- (a) These chemicals have many important commercial uses, such as paint additives, pesticides, and gasoline additives. Hundreds of premanufacture notice (PMN) forms have been submitted to the EPA for a wide variety of new compounds for new uses.
- (b) They constitute a biologically important class of chemicals, being involved in some of the most important life functions (e.g., photosynthesis in plants and oxygen transport in blood). Some highly toxic compounds (e.g., methyl mercury) can be formed in soils and sediments by the action of microorganisms.
- (c) Organometallics of various types appear to play a significant role in the mobility and bioavailability of metals in the environment. In particular, the interaction of metals with humic and fulvic acids is of prime interest.
- (d) This class of chemicals was excluded from the handbook on organic chemicals.

We propose to cover three subgroups of organometallics: (1) non-ionic organometallic complexes, (2) ionic organometallics, and (3) mixed complexes. (The necessity for the third subgroup is in question; this will be resolved in Phase II.) An introductory section will help the user classify specific compounds into these subgroups.

The following sections provide additional background information on these chemical classes and our proposed coverage of them in the Phase II handbook.

(2) Background

- Generic Types: Interactions between organic and metallic species can occur through a variety of different bonding mechanisms, which generally define the nature of the resulting complex. In particular, the degree of charge separation and polarizability of the organic-metal bond are extremely important in defining the overall physical and chemical characteristics of the compounds. These, in turn, determine the predominant pathways which the compound will follow if released to the environment.
- Differences: It may be possible to treat many organometallic species as if they were simply members of the more classic "organic" or "inorganic" categories of

compounds. Measurement of a property such as the octanol/water partition coefficient may be sufficient to indicate in which category a particular chemical belongs. The major deviation from such an approach occurs in the consideration of organometallics containing ionic bonds: the parameters that affect the distribution of inorganics in the environment may be different for these highly polar compounds, due primarily to the effects of the organic portion of the complex. These similarities and differences would be addressed in the following sections.

- Examples: Organometallics of recent interest include those which have been assigned TLVs (see Table 14), those on the RCRA listing of Hazardous Wastes (Table 15), Agricultural Chemicals (Table 16), and Section 4 and 5 of TSCA Chemicals (Tables 17 and 18). (Please note that the nomenclature used in these tables reflects the nomenclature used in the sources listed and may be inconsistent with the current rules for terminology.)
- Other Sources: Texts describing organometallics and property compilation reviews may also provide additional information on compounds of concern.

(3) Non-ionic Organometallic Complexes

- Sigma- and Pi-bonded Complexes: Many metal-organic complexes contain only metal-organic sigma or pi bonds. Complexes containing only metal-organic sigma bonds include a substantial number of species which have become available in recent years. Although the normal two-electron covalent bond does appear to be present, it may have considerably more ionic character (polarity) than that of typical carbon-carbon bonds.

The compounds in this category (i.e., complexes with metal-organic sigma bonds) include those with available electron systems in the organic fragment (e.g., metal carbonyls) as well as simple metal-alkyl species (e.g., tetraethyl lead). The reaction pathways available to such compounds may primarily be a function of the metal present (e.g., main group vs. a transition metal), although other groups associated with the metal (e.g., a pi bonded substituent) and the structure of the σ -bonded organic species itself are likely to be important. (Methylcyclopentadienyl manganese is one example of a complex with both a metal-organic sigma bond ($\text{CH}_3\text{-Mn}$) and a metal-organic pi bond [cyclopentadiene-Mn]. In this case the reaction pathways may be a function of Mn, the $\text{CH}_3\text{-M}$ sigma bond or the cyclopentadiene-Mn pi bond.) The ⁿ organometallic compounds that truly fall into this category -- i.e., those that contain real "sigma" bonds -- are generally very

TABLE 14

ORGANOMETALLICS WITH THRESHOLD LIMIT VALUES

Ethyl Silicate
 Iron Pentacarbonyl
 Manganese Cyclopentadienyl Tricarbonyl
 Mercury Alkyl Compounds
 Methyl Silicate
 Nickel Carbonyl
 Sodium 2,4-dichloro-phenoxyethyl sulfate
 Sodium Fluoroacetate
 Tetraethyl Lead
 Tetramethyl Lead
 Tin Organic Compounds
 Zinc Stearate

Source: American Conference of Governmental Industrial Hygienists,
 Threshold Limit Values for Chemical Substances in Work Air,
 Adopted by ACGIH for 1982, Cincinnati, OH, 1982.

TABLE 15

ORGANOMETALLICS ON RCRA LISTING OF HAZARDOUS WASTES

Acetic Acid, lead salt
 Acetic Acid, thallium (I) salt
 Dichlorophenyl Arsine
 Diethyl Arsine
 Ferric Dextran
 Fluoroacetic Acid, sodium salt
 Mercury Fulminate
 Phenyl Dichloroarsine
 Phenylmercuric Acetate
 Tetraethyl lead
 Selenourea (carbamimido selenoic acid)

TABLE 16

ORGANOMETALLICS USED AS INSECTICIDES, FUNGICIDES,
HERBICIDES, FUMIGANTS, GROWTH REGULATORS, REPELLENTS, AND RODENTICIDES

Aluminum tris-o-ethyl phosphonate
Ammonium Methanearsonates (t-octyl or t-dodecyl)
Ammonium Sulfamate
Cadmium Succinate
Copper salts of fatty and rosin acids [20-25% copper abietate, 8-12%
copper linoleate, and 10-15% copper oleate; $(R-CO_2)_2-Cu$]
Cupric cyclopentanecarboxylate
Copper-8-quinolinolate (Copper-8-hydroxyquinolate)
Ferric Methanearsonate (Ferric Ammonium Salt)
PhenylMercuric Acetate
Potassium Sorbate
Sodium Lauryl Sulfate
Sodium Monofluoroacetate
3-Trifluoromethyl-4-nitrophenol, Sodium Salt
Disodium Methanearsonate
Monosodium Acid Methanearsonate
Dimethylarsenic Acid (Sodium Salt)
Sodium N-Methyldithiocarbamate Dihydrate
Sodium di-nitro-o-cresylate
Sodium Salt of 2,3:4,6
bis-O-(1-methylethylidene)-alpha-L-xylo-2-hexulofuranosonic Acid
Sodium Sesqui Salt of [N-(Phosphonomethyl) Glycine]
2-Chloroethyl-tris (2'-methoxy-ethoxy) Silane
2-Chloroethyl Methyl bis (phenylmethoxy) Silane
Triphenyltin Hydroxide
Triphenyltin Acetate

Source: W.T. Thomson, Agricultural Chemicals, Book I, II, III, or IV
1983-194 Revision, Thomson Publications, Fresno, CA.

TABLE 17

ORGANOMETALLICS LISTED AS TSCA SECTION 4 CHEMICALS

Alkyltin compounds
 Calcium naphthenate
 Cobalt naphthenate
 Dibutyltin bis(isooctyl maleate)
 Dibutyltin bis(isooctyl mercaptoacetate)
 Dibutyltin bis(lauryl mercaptide)
 Dibutyltin dilaurate
 Dimethyltin bis(isooctyl mercaptoacetate)
 Lead naphthenate
 Monobutyltin tris(isooctyl mercaptoacetate)
 Monomethyltin tris(isooctyl mercaptoacetate)

TABLE 18

ORGANOMETALLICS LISTED AS TSCA SECTION 5 CHEMICALS
 (selected examples)

Substituted phenyl azo substituted naphthalenedisulfonic
 acid, sodium salt
 Metal polyisobutenylsuccinate
 Alkoxyethyl polysilazanes
 An organic complex of a halogenated metal
 Product of alcohol, halogenated metal, organic complex of
 halogenated metal
 Metal amine propanol complex
 Calcium sodium ethylenediamine tetrakis (methylene
 phosphate)
 Alkylthio metallic mercaptan
 Cobalt complex-1(hydroxynitrophenyl-azo)(substituted) phenyl
 pyrazolonesl sodium salt
 Chromium complex of a substituted phenolazophenylpyrazolone
 Iron complex of substituted phenolazoresorcinol
 Zinc-containing alkenyl carboxamide

similar in physical and chemical characteristics to organic compounds, and many of the properties of importance may therefore be the same.

One major factor that must be considered is the relative ease (compared to carbon-carbon bonds) with which some of these σ -bonded species undergo reaction at the σ bond. Such reaction considerations may be important in determining environmental pathways of importance (e.g., photolysis, hydrolysis).

The second type of non-ionic complex, generally represented as containing metal-organic π bonds, is not found as a discrete species among purely organic (i.e., carbon-hydrogen) compounds, although organic charge-transfer complexes are closely analogous. In these complexes, the π electrons available from an organic species interact by overlap with the large atomic orbitals (p,d, and in some cases, f orbitals) of the metal atom. Many such compounds have been prepared from transition metals, apparently making extensive use of the available d orbitals in these atoms. Cyclopenta-dienylmanganese tricarbonyl is an example of one such species.

The coordinated π electron system of the organic ligand is generally represented as forming a stable complex with the metal through two interdependent components:

- Overlap of the π electrons of the organic olefin with a σ -type acceptor orbital of the metal atom, and
 - "Back-bonding," or donation of electron density from filled metal orbitals (the d, f, or hybrid orbitals) into antibonding orbitals of the organic π electron system. The bonds thus formed in these types of complexes are quite stable and impart physical and chemical characteristics similar to those of organic compounds. They may therefore also be addressed in a manner very similar to that used for the estimation of properties of organic compounds.
- Interchange: Two characteristics that must be evaluated, however, are the ability of many of these complexes to exchange organic ligands and the relative ease with which transient metal-hydrogen σ bonds can be formed (a property which is used in many catalytic applications).
 - Properties of Concern: As noted above, these two types of non-ionic organometallic compounds may have physical and chemical characteristics similar to those of organic compounds. Their environmental properties of interest will therefore also be similar and can be estimated in the same

way. We propose to provide the Handbook user with guidance on the estimability of the following key properties:

Equilibrium
Partitioning

Octanol-water Partition Coefficient
Water Solubility
Soil Adsorption Coefficient
Bioconcentration Factor
Vapor Pressure

Degradation

Dissociation
Hydrolysis
Oxidation/Reduction

To the extent possible, we will use the general estimation techniques described in the organics handbook. In some cases -- e.g., the estimation of vapor pressures from boiling points -- recent tests have shown that the estimation equations derived for organics can also be applied to organometallics. Most of the property correlations will presumably hold for the class of neutral organometallics. These relations will be tested with available data, and recommendations (and examples) will be provided to the user.

Estimation of octanol-water partition coefficients from fragment constants does not appear to be possible at present because of the lack of measured data from which fragment constants can be derived. If a reasonable amount of such data can be collected, we will attempt to calculate appropriate $\log K_{ow}$ fragment constants for metals in these compounds.

It is not clear what guidance (or estimation methods) can be provided on degradation mechanisms and associated rate constants. However, because it is important to describe the stability of the metal bonds (especially those to carbon), we will provide at least a qualitative discussion.

(4) Ionic Organometallic Complexes

- General: Compounds that contain a true ionic bond, i.e., one in which an electron is donated to one of the two species involved in the bond, include those with organic cations (e.g., substituted quaternary ammonium salts) and organic anions (e.g., sodium benzoate). This generic category can also include chelates and coordination-type complexes to metal ions, in which the organic species may or may not be negatively charged (e.g., metallic cation ethylenediamine tetraacetate complexes and metallic cation-amine-anion complexes). Most of these ionic organometallic compounds are complex inorganic salts and may be amenable to similar treatment.

- Properties: Although many of the properties of these compounds that are important to determine may be the same as those of inorganic salts, one major difference must be recognized: the organic character of the compound may affect some of the likely environmental pathways for the species. For example, the highly organic character of complexes such as the sodium salts of the linear alkyl benzene sulfonates or metallic salts of fulvic and humic acids may well increase their tendency to be concentrated in biological processes, as compared with simple inorganic salts. Specifically, the organic nature of the associated salt may permit it to pass through membranes that might not readily transmit species such as sodium chloride. Thus, the octanol/water partition coefficient may be of particular interest for these compounds. Other properties must also be evaluated for their importance.

We will attempt to collect and tabulate data on properties that reflect the inorganic/ionic nature of these compounds. The properties covered will be those described in Part I of the proposed Phase II handbook. In addition, we will explore the extent to which the estimation methods for environmentally important properties of organic chemicals apply. These include, for example, octanol-water partition coefficient, soil adsorption coefficient, bioconcentration factor, and various degradation rate constants. However, the ionic character of this class of organometallics may militate against such estimation procedures, since they were developed primarily for neutral species.

(5) Mixed Complexes

It is not currently clear whether or not it will be necessary to form a third category composed of compounds that have both sigma or pi and ionic bonds, or even ionic compounds with extensive organic character (e.g., fulvic acid salts). These compounds may require special treatment, since they are not typical organic or inorganic species.

(6) Problem Areas

We expect at least two problems in covering organometallics. One is the difficulty of categorizing them by the nature of the metal bonds; the ionic or non-ionic (sigma and pi bond) nature of these chemicals is not always easy to determine simply by looking at the structural formula. One or more property values (e.g., solubility) may be required to distinguish the classes. The second problem is the lack of data; we do not expect to find much data except in limited areas (e.g., methylmercury and organotins).

APPENDICES

At present, we expect to include four appendices in the Phase II Handbook. A brief description of each is provided below.

A. SOURCES OF MEASURED DATA

The "organics" handbook contained an appendix that listed important compilations of measured data. An initial discussion was followed by a matrix (see Figure 3) listing properties of interest in the left-hand column and about 20 reference numbers across the top row. A dot was placed in the appropriate matrix element if the reference contained significant compilations of data for the indicated property. A final right-hand column for each property allowed the listing of additional properties of interest. The matrix was followed by the list of references. We propose to prepare a similar appendix for the Phase II handbook.

B. NATURAL/BACKGROUND CONCENTRATIONS OF ELEMENTS AND OTHER INORGANIC SPECIES

Elements and inorganics exist in the environment because they occur naturally and/or because they have been dispersed in the various environmental media as a result of production, use, and disposal. The environmental media of concern and the compartments in each of the media are shown in Table 19. Data on natural/background concentrations will be provided for elements and inorganics in these compartments for non-polluted and polluted areas, and also for areas near natural sources.

Also, we will provide data on concentrations of elements and inorganics in sludges from commonly disposed wastes, e.g., sludges from wastewater treatment and flue gas cleaning and desulphurization wastes.

C. DESCRIPTION OF SOIL TYPES AND PROPERTIES

Soil types may be classified under two systems:

- The Unified Soil Classification System (USCS)
- U.S. Department of Agriculture (USDA) soil classes

These are textural classes, based on the particle size of the soil grains. The USDA textural classification chart is shown in Figure 4, and a comparison of the USCS and USDA particle-size scales is shown in Figure 5. Examples of the USCS groups are shown in Table 20.

Compilations of Data for Common Properties of Organic Chemicals

Property	Source (Ref. No.)																				Other Ref.
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Solubility in Water	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21
Acid/Base Dissociation	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21
Boiling Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Heat of Vaporization	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	23
Vapor Pressure	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	24
Diffusion Coefficient	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	24
Flash Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22, 25
Density	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22, 25
Surface Tension	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22, 25
Interfacial Tension	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22, 25
Viscosity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Heat Capacity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21, 25, 26
Thermal Conductivity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	26
Dipole Moment	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Refractive Index	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Melting Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	26
Heat of Fusion	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	26
Critical Properties	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	25-28
Temperature	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Pressure	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Volume	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Critical Compressibility	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

Figure 3 Example of Matrix for Sources of Measured Data

TABLE 19
NATURAL/BACKGROUND CONCENTRATIONS OF ELEMENTS
AND OTHER INORGANIC SPECIES

<u>1. AQUATIC</u>	<u>Natural/Background Concentrations</u>
<u>1.1 Water</u>	(Data to be provided)
Marine	
• Coastal - non-polluted polluted near natural sources	
• Deep Ocean	
Freshwater	
• Streams and Rivers - non-polluted polluted near natural sources	
• Lakes and Reservoirs - non-polluted polluted near natural sources	
<u>1.2 Sediment</u>	
Marine	
• Coastal - non-polluted polluted near natural sources	
• Deep Ocean	
Freshwater	
• Streams and Rivers - non polluted polluted near natural sources	
• Lakes and Reservoirs - non-polluted polluted near natural sources	
<u>1.3 Biota</u>	
Marine	
• Coastal - non-polluted polluted near natural sources	
• Deep Ocean	
Freshwater	
• Streams and Rivers - non-polluted polluted near natural sources	
• Lakes and Reservoirs - non-polluted polluted near natural sources	

TABLE 19 (continued)

Natural/Background
Concentrations2. LAND2.1 Rocks and Soils

Location -	non-polluted polluted near natural sources
Type of Rock - or Soil	sedimentary igneous metamorphic other
Land - Use -	cropland non-cropland urban suburban rural

2.2 Terrestrial Biota

Vegetation -	non-polluted polluted near natural sources
Mammals -	herbivores omnivores carnivores

3 AIR3.1 Troposphere

Non-polluted, e.g. rural areas or remote oceanic areas	-vapor -associated with particulates
Polluted, e.g. urban areas	-vapor -associated with particulates
Near Natural Sources	-vapor -associated with particulates

3.2 Stratosphere4. SLUDGES4.1 Municipal Wastewater Treatment Sludges4.2 Important Industrial Waste Sludges

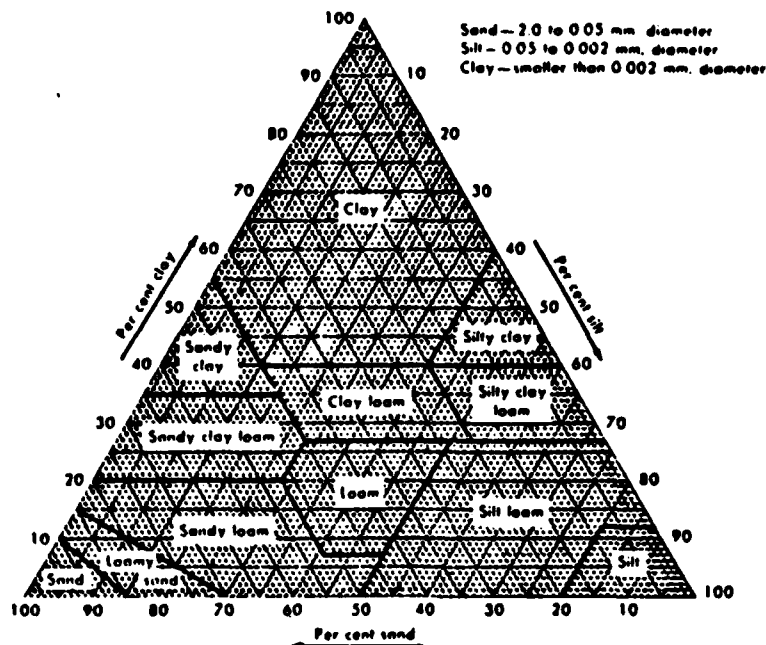


Figure 4 USDA Textural Classification Chart

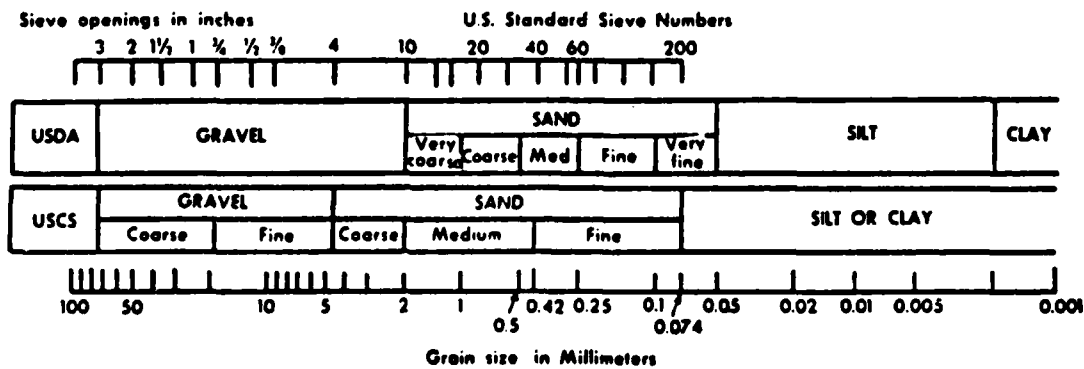


Figure 5 Comparison of USCS and USDA Particle-size scales

Source for Figures 4 and 5: Lutton, R.J., "Evaluating Cover Systems for Solid and Hazardous Waste," Report No. SW-867, U.S. Environmental Protection Agency, Office of Solid Wastes Washington, DC, September, 1982.

TABLE 20

UNIFIED SOIL CLASSIFICATION SYSTEM

<u>Group Symbol</u>	<u>Soil Description</u>
GW	Well-graded gravel and gravel-sand mixtures. Little or no fines.
GP	Poorly graded gravels and gravel-sand mixtures. Little or no fines.
-	-
-	-
-	-
-	-
PT	Peat and other highly organic soils.

The soil properties of interest are:

- Porosity (air-filled and total)
- Tortuosity
- Particulate surface area (area per unit weight)
- Bulk density
- Mineralogy
- pH
- Cation exchange capacity
- Adsorptive capacity
- Moisture content (in unsaturated zone)
- Organic carbon content (weight percent basis)
- Oxygen content
- Temperature
- Microbiological population density (and type(s)).
- Nutrient availability

The first four of the above properties are related (in varying degrees) to the type of soil.

Nevertheless, the values of these properties are not unique to each soil type. We will describe the relationship(s) of soil grain size to these properties and, as far as possible, provide ranges for the property values in a matrix of soil type versus soil property.

Other properties are dependent on factors other than grain size, such as depth of the soil layer of concern, the soil zone, or the mineralogy of the soil. We will describe these dependencies qualitatively and develop tables showing the effect of depth, soil zone, etc. on typical ranges of values for each property.

D. POLLUTANT CRITERIA OR STANDARDS

Pollutant criteria or standards of concern are administered by several agencies, primarily the Environmental Protection Agency, the Occupational Safety and Health Administration, the Food and Drug Administration, and the Department of Transportation.

Numerous regulations affect inorganics and organometallics. A sample of the standards and criteria are shown in Table 21.

We will develop a quick-reference matrix showing the standards/criteria which are applicable to particular inorganics/organometallics. The beginning of such a matrix is shown in Table 22.

Summary tables will be prepared for each of the more important standards and criteria showing the inorganics/organometallics of concern and the value of the corresponding standard or criterion.

Table 21

REGULATIONS (STANDARDS AND CRITERIA) AFFECTING
INORGANICS AND ORGANOMETALLICS

Air

National Primary and Secondary Ambient Air Quality Standards
Fuels and Fuel Additives Regulations
National Emission Standards for Hazardous Air Pollutants
Stationary Source Performance Standards

Water

Water Pollution Effluent Guidelines and Standards for Point Source
Categories
National Interim Primary Drinking Water Regulations
National Secondary Drinking Water Regulations
National Pollutant Discharge Elimination System, Criteria and
Standards
Water Quality Standards and Criteria
Toxic Pollutants Effluent Standards
Underground Injection Control Program, Criteria and Standards

Pesticides

Animal Feeds, Pesticide Tolerances
Food Additives, Pesticide Tolerances
Federal Insecticide, Fungicide, and Rodenticide Act
Pesticide Chemicals: Tolerances and Exemptions from Tolerances in or
on Raw Agricultural Commodities

Solid Wastes

Hazardous Waste Identification and Listing

Occupational Safety and Health

Agriculture Industry, Occupational Safety and Health Standards
Occupational Safety and Health Standards
Pesticide Programs, Agricultural Pesticides, Workers Protection
Standards
American Conference of Governmental and Industrial Hygienists

Table 21
(continued)

Food and Drugs

Animal Foods and Drinking Water, Food Additives
Indirect Food Additives
Food Packaging Materials

Transportation

Hazardous Materials Transportation
Transportation of Explosive
Interstate Commerce Commission Classifications

Others

WHO and FAO Recommended Maximum Acceptable Daily Intake

Table 22

STANDARDS/CRITERIA APPLICABLE TO INORGANICS AND ORGANOMETALLICS

<u>Inorganic/ Organometallic</u>	<u>Standard or Criterion</u>	
	<u>Drinking Water Standards (40 CFR 141, 143)</u>	<u>Hazardous Air Pollutant (40 CFR 61)</u>
Arsenic	X	
Abestos		
Barium	X	
Beryllium		X
Mercury	X	X

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